DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
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By H. H. Peters and F. P. Phelps

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BY

H. H. PETERS, Technologist
F. P. PHELPS, Associate Physicist
Bureau of Standards

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ABSTRACT

In the vast bibliography of Beer's law there occur only scant references to the absorption spectrum of definitely specified types of sugar sirups. No systematic investigation of absorption spectra of different types of solutions, prepared by different chemical methods from the various grades of technical sugar products, either beet or cane, appears to have been undertaken at any time previous to this investigation by the Bureau of Standards. Therefore, the exceedingly great difficulties inherent in any attempt to gauge the true color value of saccharine solutions by means of precise spectrophotometric methods have heretofore not generally been fully appreciated. These difficulties arise because of the different degrees of optical inhomogeneity of such solutions. Yet the precise evaluation of color is an indispensable necessity for commercial and sugar technological reasons. In order to avoid misunderstandings and confusion, the nomenclature and terminology of precision photometry are given separately from the rest of the paper.

A spectrophotometric study of absorption spectra of sugar solutions led to the discovery that any variation in chemical methods of preparation and clarification of solutions for an optical precision analysis causes, in turn, variations in transparency and observed light intensities. The true color value of the solute appears rather doubtful and seems to be attainable only after continued and extended research. This paper contains the detailed description of an improved method of preparation and clarification. The latter aims at the production of stable degrees of transparency and dispersion of the colloidal dispersoids. A discussion of spectrophotometric data, including certain important ratios, follows the chemical part. The color value of the solute is defined in terms of a unit quantity of saccharine dry substance by the spectrocolorimetric equivalent of intensity and quality of absorption at separate wave lengths, which at λ 560 mμ becomes a measure of color and concentration of coloring matter over the full spectrum.

A series of papers to follow this paper will present further analytical details of the investigation in its chemical and optical aspects.

CONTENTS

Part I.—COLOR NOMENCLATURE IN THE SUGAR INDUSTRY

In the past few years the importance of the study of sugar products with respect to their color qualities has become more and more fully recognized as adequate methods of estimation and interpretation of the phenomena encountered have been developed. One of the more urgent needs in this phase of the sugar industry is the establishment of a recognized and uniform nomenclature and system of standards. Much progress has been made in this direction in other fields of color work. Since color and its measurement in the sugar industry is based upon exactly the same fundamental concepts and principles as in other branches of colorimetry, and especially in the field of spectrophotometry, it is logical that the progress already made in the development of a system of nomenclature in those other fields be made use of in the sugar industry.

In the work at the Bureau of Standards on color phenomena in sugars the recommendations contained in the various reports of the Committee on Standards and Nomenclature, and Progress Committees of the Optical Society of America have been adopted. Special care has been taken to conform to the recommendations of the Committee on Spectrophotometry (J. O. S. A. and R. S. I., **10,** pp. 169–241; February, 1925) and the Committee on Colorimetry, Preliminary Draft, 1919,[1] and subsequent reports of this latter committee published from time to time in J. O. S. A. and R. S. I., insofar as those recommendations adequately cover the ground. In certain cases, however, it has been found necessary to coin new terms and symbols. Where this has been necessary the new symbols and terms have been selected and defined in such a manner as to cover the desired ground and at the same time be an extension of, and not in conflict with, the recommendations contained in the committees' reports.

To one not thoroughly familiar with the subject the elaborate and extensive system with its fine distinctions of meaning to be hereinafter set forth may appear somewhat pedantic and academic. Not so, however, to him whose daily work is in this field, for he is continually inconvenienced and annoyed by the circumlocution and misunderstandings occasioned by lack of suitable terms and symbols to express his ideas and findings cogently and without ambiguity.

It will be noted in the list of terms below that there are many that are not explicitly used in the color work on sugar products. The terms that are most used in experimental sugar work are relatively few in number ($\mathbf{T}$, $\mathbf{t}$, $-\log \mathbf{T}$, $-\log \mathbf{t}$, c, b, λ, Q, n, as defined below). The others are necessarily given for the purpose of precisely defining these terms and to bring out the small but important differences between them and certain other similar terms.

[1] Unpublished, but may be consulted in the Bureau of Standards library.

In the case of homogeneous light passing through homogeneous substances, such as a plane parallel polished plate of glass, we have the following terms,[2] all being functions of wave length:

E = radiant energy (of light source).

E_1 = radiant energy incident upon the first surface.

E' = radiant energy reflected at the first surface.

E_I = radiant energy transmitted by the first surface.

E_2 = radiant energy incident upon the second surface.

E'' = radiant energy reflected at the second surface.

E_{II} = radiant energy transmitted by the second surface.

$E_I = E_1 - E'$.

$T = \frac{E_{II}}{E_1}$ = transmission. It is the fraction of the incident light which is transmitted, and not lost either by reflection or absorption.

$\mathsf{T} = \frac{E_2}{E_1 - E'} = \frac{E_2}{E_I}$ = transmittance; that is, the transmission after correcting for losses by reflection.[3] The transmittance per unit of thickness, which is called transmissivity, t, may be calculated from the transmittance, T, for any thickness, b, by means of the relation

$t = \sqrt[b]{\mathsf{T}}$ = transmissivity, which is known as Lambert's law. No exceptions to this law have ever been noted.

$\mathsf{A} = 1 - \mathsf{T}$ = absorbance.

In the case of transparent solutions:

$T_{sol.}$ = transmission of a given cell containing the solution.

$T_{sov.}$ = transmission of the same (or a duplicate) cell containing pure solvent.

$\mathbf{T} = \frac{T_{sol.}}{T_{sov.}} = \frac{\mathbf{T}_{sol.}}{\mathbf{T}_{sov.}}$ = transmittancy; that is, the transmission after correction for reflection at the surfaces and for absorption, if any, by the pure solvent.

Since the absorption of pure water is negligible for our purposes, $\mathbf{T}$ has practically the same significance as T above. The symbols $\mathbf{T}$, $\mathbf{t}$, $\mathbf{A}$, referring to solutions, are distinguished from T, t, A, referring to solids (or homogeneous substances), in handwriting and typewriting by underscoring the former, and in printing by the use of bold-face type as is recommended in the spectrophotometry report (J. O. S. A. and R. S. I., February, 1925). Since in all cases we compensate for losses by reflection by the use of a water cell (or one containing a colorless sucrose solution) exactly similar to the cell containing the solution to be measured, we have to do only with the

[2] Committees' reports referred to above.

[3] For a more detailed treatment of the relation between T and T see B. S. Tech. Papers No. 119, pp. 9–12, and No. 148.

transmittancy, **T**, and not at all with the transmission, T, or the transmittance, T.

t = specific transmissivity = transmittancy reduced to unit conditions as regards thickness and concentration; **t** differs from t above in that **t** takes into account concentration as well as thickness.

b = thickness (cm) of the absorbing solution.

c = concentration (grams saccharine dry substance per 1 cc of solution). c refers exclusively to the original colored dry substance which consists of sucrose + nonsugar + coloring matters.

$$\mathbf{t} = \sqrt[cb]{\mathbf{T}} \text{ or } -\log \mathbf{t} = \frac{1}{cb}(-\log \mathbf{T}) = \text{(Lambert's-Beer's law)}.^{4}$$

$-\log \mathbf{t}$ is a measure of the coloring power—that is, intensity of absorption—of the unknown amount of coloring materials associated with 1 g of saccharine dry substance.

$$\mathbf{A} = 1 - \mathbf{T} = \text{absorbancy}.$$

Since the transmissivity t and the absorption coefficient or exponent are related[5] according to the equation $t = e^{-i}$, where i, the absorptive exponent, depends upon the nature of the substance and the wave length, it is evident that independent of the original use of the minus sign before the log t (log transmissivity) as a matter of convenience, $-\log t$ is the absorptive index and has a definite physical significance.

$-\log \mathbf{t}$ = the specific absorptive index.[6]

λ = wave length.

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[4] This law may or may not be valid for different types of coloring matters in solution under the conditions obtaining in the sugar industry. Under these conditions it is valid at best only within rather narrow confines as to concentration and transparency. However, it was found to be valid for several hundred absorption spectra of technical sugar products ranging from white sugar to final molasses, but only upon condition that stable transparency was produced in the solutions. This was accomplished by an improved process of colorimetric clarification which is described in the following paper.

[5] Preston, Theory of Light, p. 470.

[6] $-\log \mathbf{t}$ in the above committee reports was defined as specific transmissive index instead of absorptive index. That specific absorptive index is the more appropriate name may be seen from the following demonstration. (See also Preston, l. c.) Using the symbols tabulated above in the case of a homogeneous solid, suppose a beam of light passes through a parallel-faced slab of thickness, b. The change (decrease) in energy, E, of the beam in passing through the infinitely thin layer, db, is given by the differential equation, $-dE = iEdb$, where i is a coefficient proportional to the absorption or absorbing power of the substance. It depends upon the nature of the substance and the wave length, but is constant for any given substance at any given wave length. It may be called the absorption coefficient or exponent, as will appear later.

Separating the terms of this equation we have $-\frac{dE}{E} = idb$. Integrating between the limits $b=o$ to $b=b$ and $E=E_1$ to $E=E_2$ as above defined, we have

$$-\log_e E \Big]_{E_1}^{E_2} = ib \Big]_o^b$$

Putting in these limits $-[\log_e E_2 - \log_e E_1] = ib$, or $-\log_e \frac{E_2}{E_1} = ib$. Since $\frac{E_2}{E_1} = \mathrm{T}$, $-\log_e \mathrm{T} = ib$, or $i = -\frac{1}{b}\log \mathrm{T} = -\log \mathrm{T}$. Therefore, $\mathrm{T} = e^{-i}$. Since i in the differential equation is the quantity which defines absorption, $-\log_e \mathrm{T} = i$ should be called the absorptive exponent and $-\log_{10} \mathrm{T} = \frac{i}{2.3026} = k$ should be called the absorptive index.

The last four gothic T's of footnote 6 should be lower case italic t's.

λ_c = wave length at the optical center of gravity of the luminosity curve. It is defined by the equation:

$$\lambda_c = \frac{\Sigma(L_\lambda \cdot \lambda)}{\Sigma L_\lambda} \text{ or } \frac{\Sigma(E_\lambda \cdot V_\lambda \cdot \mathbf{T}_\lambda \cdot \lambda)}{\Sigma(E_\lambda \cdot V_\lambda \cdot \mathbf{T}_\lambda)}$$

$L_\lambda = E_\lambda \cdot V_\lambda \cdot \mathbf{T}_\lambda$ = relative spectral luminosity of the layer of solution whose transmittancy is $\mathbf{T}_\lambda$.[7]

$\sum_{\lambda=0}^{\lambda=\infty} L_\lambda$ = luminosity integral obtained by summation at intervals of 10 mμ.

V_λ = relative visibility (spectral luminous sensitivity of the eye).

mμ = 0.001μ = 0.000,000,001 meter = millimicron, a measure of λ.

λ = 560 mμ is the wave length at the optical center of gravity of the luminosity curve for unit quantity of coloring material ordinarily occurring in sugar products.

$$Q = \text{absorption ratio} = \frac{\text{specific absorptivity at } \lambda}{\text{specific absorptivity at } \lambda = 560} = \frac{-\log \mathbf{t}_\lambda}{-\log \mathbf{t}_{\lambda 560}}$$

$$R_{\lambda_1} = \frac{\text{specific absorptivity at } \lambda}{\text{specific absorptivity at any chosen } \lambda} = \frac{-\log \mathbf{t}_\lambda}{-\log \mathbf{t}_{\lambda_1}}$$

$R_{\lambda 1}$ differs from Q only in the choice of the wave length used as the reference point, some wave length other than 560 being used.

Q (and R_λ) measures the quality of absorption of a solution; that is, the relative intensities of absorption of the solution for different parts of the spectrum.

$$R_s = \frac{-\log \mathbf{t} \text{ of one solution at any } \lambda}{-\log \mathbf{t} \text{ of another solution at the same } \lambda},$$

the relative absorbing power of two different solutions at some particular wave length.

1 Absorption unit at a given wave length = $-\log \mathbf{t}_1$ = the $-\log \mathbf{t}$ of one unit of coloring matter; that is, the coloring matter associated with 1 g of the standard sugar or the optically equivalent amount associated with some other sugar product.

There is therefore no *fixed* absorption "unit" for all wave lengths. The magnitude of the absorption "unit," therefore, varies with wave length in the same manner as the $-\log \mathbf{t}$ of the colored solution which is to be measured.

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[7] The values of E_λ. V_λ used throughout by the present authors are those of Priest's tentative standard of average noon sunlight at Washington. For further discussion of E, V, λ_c, L_λ, ΣL_λ, etc., see J. O. S. A. and R. S. I., **4**, p. 388; 1920; ibid, **7**, p. 1175; 1923; ibid, **7**, p. 1188; 1923; ibid, **8**, pp. 173–200; 1924; ibid, **9**, p. 403; 1924; ibid, **10**, p. 292; 1925; B. S. Sci. Paper No. 303; 1917; B. S. Sci. Paper No. 417; 1921; B. S. Sci. Paper No. 475; 1923; B. S. Tech. Paper No. 119, p. 18; 1919.

One color degree is the integrated (sum total) effect for the visible spectrum of one absorption "unit" at each wave length. One unit of coloring matter evokes a color sensation of one color degree and is measured by its integral (sum total) absorption $\left(\sum_{\lambda=440}^{\lambda=700} -\log \mathbf{t}_1\right)$ over the visible spectrum. The visual effect of this is represented by $\sum_{\lambda=440}^{\lambda=700}$ V. E. $\mathbf{t}$ the luminosity curve of the transmitting layer of unit thickness.

n = the number of units of coloring matter corresponding to n color degrees and n absorption units.

$$n = \frac{-\log \mathbf{t}_{\lambda=560} \text{ (of sample)}}{-\log \mathbf{t}_{1\lambda=560} \text{ (of standard)}} = \frac{-\log \mathbf{t}_{\lambda=560} \text{ (of sample)}}{0.00485}.$$

The sum total absorption of one unit of coloring matter, $\sum_{\lambda=440}^{\lambda=700} -\log \mathbf{t}_1$, is defined as equivalent, colorimetrically, to the common absorption unit $-\log \mathbf{t}_1$, measured at $\lambda = 560$, the wave length at the optical center of gravity of its luminosity curve. The numerical value of $-\log \mathbf{t}_1$ at $\lambda = 560 = 0.00485$.

n is the number of units of coloring matter in 1 g of saccharine dry substance.

Part II. COLORIMETRIC CLARIFICATION OF TURBID SUGAR SOLUTIONS[1]

I. INTRODUCTION

The development of color measuring devices has introduced into industrial sugar laboratories photometers for the analysis of color through the measurement of absorption at separate points or regions of the spectrum. In consequence of the higher precision attainable with these instruments, greater care and accuracy are required in every detail of laboratory practice. The advantageous use of a precision instrument is dependent, among other things, upon the application of improved methods in the preparation of transparent solutions from turbid solutions of technical sugar products. It has been found through the systematic application of a spectrophotometer that the well-known method of colorimetric clarification, which has been in practically universal use in the colorimetry of sugar products since 1860, is entirely inadequate and is not to be considered a precision method. A reorganization of commonly held conceptions on the efficacy of colorimetric clarification is necessary. The accuracy of all determinations of absorption and of color concentration is dependent upon the validity of Lambert's-Beer's law, which is a fundamental law of all photometry and colorimetry of sugar products and which in turn is dependent upon several factors.[2] Most important among these are the choice of (*a*) a correct dry substance concentration (approximately 0.70 g d. s. per 1 cc), and (*b*) the degree and stability of transparency of the solution. The degree of dispersion of the colloidal, color-bearing nonsugar changes rapidly upon dilution with water and is also easily affected by faulty chemical methods of preparation.

It is necessary to discriminate between two types of analytical preparation—the customary one and the one which is described below. The type of analytical preparation which is recorded in textbooks of sugar analysis and in the older bibliography of the subject is here referred to as the older method of analytical preparation for colorimetric analysis. It has been found necessary to discard this method in its entirety. In contradistinction to this

[1] The analytical method of preparation herein described is substantially the same as that presented before the sugar division of the American Chemical Society at Rochester, N. Y., in 1921, under the title "The Determination of Color and Decolorization of Technical Sugar Products."

[2] See G. Rudolph, Sammlung Chem. and Chem. Techn. Vortrage, **9**, p. 1; 1904; O. Scarpa, Koll. Zeits., Supplement II, **50**, 1908: Is Beer's law valid for colloidal solutions?

well known and commonly practiced method, that described herewith has been found satisfactory at the present stage of development. It should always be used if precision instruments are to be employed and is also preferable if less accurate instruments are utilized. For an illustration of the magnitude of the differences between the two methods see Table 1, page 294.

Common filtration methods and filter media are employed in the present method as well as in the older one. While the concentrated sugar solutions are filtered under reduced pressure by the common type of laboratory filter pump, neither pressure filtration nor ultrafiltration are discussed. These phases of the problem will be taken up in a later paper.

The process of colorimetric clarification to be described consists of three distinct and separate operations:

1. The preparation of turbid solutions by a careful attention to analytical detail, using water as the solvent of dry substance under specified conditions.

2. The preparation of correct degrees of color concentration by using, if necessary, a concentrated diluent of color in place of water. This concentrated diluent is a carefully prepared decolorized solution of white granulated sugar, beet sugar being used for beet-sugar products and cane sugar for cane-sugar products because of the difference in the pH values.[3]

3. The preparation of transparent filtrates from the turbid solution by an improved process of clarification and filtration.

The preparation of transparent filtrates of appropriate dry substance and color concentrations is dependent upon the use of the following auxiliary material:

1. Optically clean asbestos fiber, to be used as (*a*) a filter medium in place of filter paper, and (*b*) a clarifying agent in place of kieselguhr. The economical use of high-grade asbestos fiber requires the rejuvenation of used asbestos pads after several filtrations.

2. A concentrated, transparent solution of recrystallized white granulated sugar which is used as a diluent of dark-colored sugar solutions in place of water.

3. Stammer ulmin solution, recommended as a guide in the adjustment of the color concentration. The degree of color concentration selected will depend upon the quality of the sugar product, the type of color measuring device, and the thickness of the plane parallel cells available. Greater familiarity with the different degrees of color concentrations which must be prepared will gradually make the use of the ulmin solution unnecessary.

4. Refractometers.—The water percentage of the optically transparent filtrates should be determined by a refractometer, the

[3] Bates, Internat. Sugar J., **22**, p, 654; 1920.

scale of which has been carefully checked by actual observations of solutions of c. p. sucrose [4] at the normal temperature of 20° C. Scale errors should be rechecked and ultimately plotted so that correct interpolated values may be obtained at any concentration, but particularly at points between 40 and 50 per cent water. It should also be noted that some of the existing types of refractometers are objectionable, being rather inaccurate for the reason that there is a lack of rigidity in the system, so that different readings may be obtained for the same charge after opening and closing the prisms. Readings should be taken only at 20° C., controlling the temperature of the prisms when necessary.

II. PREPARATION OF AUXILIARY MATERIAL

1. PREPARATION OF ASBESTOS FIBER FOR OPTICAL ANALYSIS

Not all grades of asbestos fiber are suitable for the preparation of solutions when precision instruments are used for the determination of absorption. Satisfactory results were obtained by using XX or XXX grade long fibered Powminco asbestos, as supplied by the Powhattan Mining Co., Woodlawn, Baltimore, Md. No study of other sources of asbestos has been made.

This grade is acid-treated and washed by the producers, but for the requirements of optical analysis the following additional treatment is necessary: Seventy-five g of the asbestos is digested on a water bath for 24 hours with 2 liters of water to which has been added 10 per cent by volume of concentrated hydrochloric acid (c. p.) and one-third as much concentrated nitric acid (c. p.). Filter on a Büchner funnel, press out the excess of acidified water, and digest repeatedly with hot water (clear tap water may be used in the beginning if free from iron or sediment). After most of the acid has been removed by several digestions and filtrations wash repeatedly by decantation in order to remove the woolly fiber which is present; then place the fiber on a fine cloth and wash continuously for about three days or longer, or washing by decantation may be continued until all foreign matter which may cause turbidity has been washed out and only the long fiber remains. The washing process may be speeded up if a centrifuge is used. Use hot distilled water in all cases as a final wash. The final wash-water should be examined in the dark room, and preferably in a plane parallel glass cell ($b=10$ or 20 cm). A strong beam of light is passed through the water, which must then appear transparent excepting a few floating asbestos specks. These may be eliminated if the water is filtered through a 200-mesh silk strainer.

[4] B. S. standard sample No. 17 was used by us.

Should the wash water at any time have been impure, the acid treatment must be repeated. The final continuous washing for several days can not be avoided, as all foreign suspended matter must be removed. Finally, dry in a dust-free air and keep in a stoppered bottle. The washed fiber is used either for the carefully prepared final filtering pads in Gooch crucibles or as a clarifying agent (in place of kieselguhr) for the turbid, impure saccharine solutions. In the latter case it may be permissible to use the less expensive A-long grade instead of the XX grade. However, in that event the two filtrates of the same solution must show the same degree of transparency.

2. FORMATION OF ASBESTOS FILTERING PADS

One and one-half to two g of dry, specially washed, long-fibered XX grade of Powminco asbestos is weighed off for each Gooch crucible of 25 cc capacity and shaken up with distilled water to produce an easy flowing mixture. A circular disk of bolting cloth silk, 200 mesh, is placed in the bottom of each Gooch crucible. The silk is held in place with a glass rod when pouring the mixture of water and asbestos fiber into the crucible. The crucible adaptor is fitted to an 8-ounce bottle which serves as a receiver for the filtrate. Use slight suction to form a thin pad, remove the crucible from the holder, and carefully examine the position of the silk from all sides. Replace the crucible in the holder and continue the gradual formation of the pad. The method of padding, as well as all other operations, should be carefully standardized, so that each of the six crucibles in the battery will have the same rate of filtration. A new series of washings of these pads is essential as a precautionary measure before actual use. Boiling-hot distilled water is poured successively into the six units of a battery of asbestos filtering pads under slight suction in such a manner as to not disturb the asbestos. The washing is continued with boiling-hot distilled water until each pad has received at least three complete washings. Examine the last wash water of each pad in the dark room, as described below. The prepared crucibles should be protected from dust. The pad itself will be over 1 cm thick in a 25 cc crucible.

3. CARE OF GLASS CONTAINERS (RECEIVING BOTTLES, PHOTOMETER CELLS, ETC.)

All glass containers, such as the bottles which are to receive the final filtrate, must be scrupulously clean. Glass containers which receive the filtrates and solutions of technical sugar products soon become coated with an oily film, so that a film of water contracts in patches over the glass surface. This film may be removed by first using chromic acid cleaning fluid and then polishing each glass

container by violently shaking with clean filter-paper pulp. Rinse thoroughly, first with tap and then with distilled water, until all receivers are clean. Store all glass cells and bottles in a dust-free container.

Eight-ounce wide-mouthed bottles are suitable for light colored sugar solutions and 4-ounce bottles for all darker colored solutions. It is most important that the outer surfaces of the photometer cells be thoroughly cleansed after filling the cell with transparent filtrate. The surface is soaped with castile soap, rinsed, wiped with soft linen, and polished with lens paper. Condensation of the breath reveals any remaining oily film which would necessitate repetition of the cleansing process.

4. PREPARATION OF A BATTERY OF ASBESTOS FILTERING UNITS

Each Gooch crucible in a battery of six (see fig. 1) is fitted to an 8-ounce wide-mouthed bottle by means of a glass adaptor and rubber sleeve, the latter connecting the adaptor to the crucible. The adaptor is passed through a 2-hole rubber stopper, the other hole being fitted with a glass tee. One branch carries a Geisler stopcock; the other branch leads to the vacuum header which leads to the central vacuum chamber. Each suction tube passing from the filter to the vacuum header and suction chamber is fitted with a glass stopcock, so that the filtering process may be interrupted for each individual unit without great interference with the continuous filtering of the other units. The central vacuum chamber is fitted with a barometer tube or other pressure gauge, so that the pressure may be known at all times when the battery of filtering pads is in actual operation. An ordinary water filter pump is sufficient for the creation of the vacuum in the system.

A further refinement in the above device will considerably facilitate the ease of operation in case one part of the battery is still used for filtering, when it is desired to start the rejuvenation of the fiber in the other parts. The filtration itself proceeds with cold liquors. In the process of rejuvenation of the fiber a quantity of vapor is produced, due to the hot wash water flashing into steam under the reduced pressure. Adulteration of the remaining filtrates by the condensation which immediately takes place in the header may occur unless a trap is added to each filter. All traps and connections introduce chances for air leaks. The construction of two vacuum headers eliminates this potential trouble very simply. One header is called the dry header or filter header; the other the vapor header. Either header may be connected to the suction tube of the filter at will by means of a three-way cock which permits the cutting in and out of any unit at any moment without interfering with the filtration process in the remaining units. The vapor header may advan-

FIG. 1.—*Battery of filters*

tageously be trapped before entering the central vacuum chamber. The latter must be of sufficient volume to counteract any violent disturbances of the pressure in the system, due to cutting in of the new cycle of a filtering unit; for instance, a Wolff bottle of 3 liters capacity is satisfactory for this purpose.

A study of Figure 1 will further assist in the construction of the filter battery from easily obtained material. When the construction of a vapor header is dispensed with, the danger from condensed vapor may be eliminated by operating the six units either all on liquor or all on rejuvenation. Nevertheless, careful attention is necessary to prevent a possible drawing over of fluid from the header into the receiver of an adjacent filtering unit. Only a system of independent traps can completely prevent this contingency.

5. REJUVENATION OF ASBESTOS

Continued observation and experience leads to the recommendation that in precision work a pad should be used but once regardless of the character of the sugar solution. However, by careful manipulation a used pad may be rejuvenated in its crucible. In any case at least 8 ounces of hot water is passed through the used pad to completely remove the sirup. All washed pads may then be rejuvenated either individually or by one common operation for all pads after removal from their crucibles. First digest for some time with a definite volume of hot $N/5$ sodium hydroxide solution and thereafter wash repeatedly with distilled water. A digestion with an equal volume of a $N/5$ hydrochloric acid solution follows. Thereafter the cleansing processes are continued with pure distilled water, just as for asbestos put into use the first time. However, should the asbestos fiber be very foul with colloidal organic matter, then a more energetic destruction of organic matter is necessary. In this case the fiber is either digested with dilute aqua regia to destroy organic matter or ignited in a muffle furnace at low red heat and subsequently treated with the dilute aqua regia and washed.

The silk should be examined with a magnifying glass from time to time. The satisfactory performance of the rejuvenated pads should be determined by the optical examination of the final washings in the dark room.

6. TREATMENT OF PADS

Asbestos pads formed through the process termed preliminary clarification will contain the matter screened out from the turbid solution. Pads of this type are washed at once with boiling-hot water and deposited in a bottle until enough have been collected to warrant rejuvenation of the fiber. The asbestos fiber of the best optical pads must not at any time be contaminated with that of these second-grade pads.

All possible precautions must be taken to keep the fiber of the high-grade final pads, for the preparation of transparent filtrates, as clean as possible. Murky, dirty liquors, such as those containing floating carbon particles or sediments from tanks, and solutions of great turbidity must undergo a preliminary clarification before filtering through a final pad. With proper care these final pads may be used several times for routine analyses. However, the most consistent results are generally obtained when new pads are used for each filtration.

Other types of filter media, such as Chamberland filters, siliceous filtering plates, alundum crucibles, etc., have not been studied sufficiently to arrive at a definite conclusion in regard to their effect upon quantitative measurement of absorption.

7. PREPARATION OF A DECOLORIZED, TRANSPARENT, GRANULATED SIRUP, TO BE USED AS A DILUENT OF COLOR

Dissolve the best quality of granulated sugar, either beet or cane, as required, in hot water to about 55 Brix; add decolorizing carbon, such as washed Norit or Darco, using an amount equal to 2 per cent of the dry substance. Digest for about 15 minutes on a water bath at a temperature from 80 to 85° C. About 10 per cent of the best grade of kieselguhr is then added to the mixture, which is then filtered under vacuum through a filter paper on a Büchner funnel. The first portions are poured back so that a clear filtrate is obtained. This filtrate is then filtered through the optically clean asbestos. Shake up the clean filtrate with the necessary amount of dry asbestos to form a good pad (about 0.75 g asbestos per 100 cc), filter and refilter several times. A layer of 200-mesh bolting silk should be placed under the pad before use. In precision analyses it may be necessary to recrystallize the resulting clear filtrate in a glass vacuum pan in the laboratory.[5] The final solution, which should be practically colorless, should be examined spectrophotometrically, and the transparency should be tested as described below. This stock sirup should not be kept indefinitely either at room temperature or in the ice box. Although its transparency may appear satisfactory, yet after a few days' storage it may be found that the specific absorptive index, $-\log t$, has increased. The absorbing power of freshly made and carefully prepared colorless sirup is so extremely small that it may be ignored even in precision spectrophotometric analyses except in the blue end of the spectrum. If absorption of colored solutions is measured in this region, then the effect of the specific absorptive indexes ($-\log t_s$) of the stock solution should be considered and if necessary taken into account when calculating the specific absorptive indexes of the sugar product in cases in which this diluent has been used.

[5] See B. S. Circular No. 44, p. 94.

8. STAMMER'S ULMIN SOLUTION: A GUIDE TO THE COLOR CONCENTRATION OR DEPTH OF COLOR

The original stock solution is prepared according to Stammer's directions (Zuckerfabrikation, Dr. K. Stammer, vol. 1, p. 750): "To 300 cc of 20 per cent sugar solution add 5 cc pure concentrated sulphuric acid diluted with 20 cc distilled water. Heat the solution for one-half hour on the water bath. Add at once to the hot solution 10 g of dry sodium hydroxide; keep at boiling temperature for 5 minutes. Cool and dilute with water to 300 cc." The solution should be kept in a dark room.

Immediately before use the stock ulmin solution is diluted in the ratio of 1 to 5. This dilute solution is here called concentration one. From this diluted ulmin solution prepare four other concentrations, called concentrations $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{16}$, diluting one volume of ulmin solution with enough water to produce 2, 4, 8, and 16 volumes of dilute ulmin solution. The choice of concentration for a given thickness of cell, b, depends upon the type of color measuring device to be used, as each instrument is most efficient for a certain range of color concentration. Thus, if a Stammer or any other colorimeter is used in which luminosities are matched with each other in diffuse daylight, the straw color recommended by Stammer is essential, as the sensibility of the eye is greatest for certain definite ranges of saturation. The straw color of sugar solutions for thickness, b, of 10 to 20 centimeters of the Stammer instrument, as recommended by Stammer, is matched by concentrations between $\frac{1}{8}$ and $\frac{1}{16}$.

If a Hess-Ives tintphotometer is used in the analysis of a colored sugar solution, then the solution in its photometer cell should match a 2 cm layer of an ulmin solution whose concentration depends upon the manner of using this type of equipment. To illustrate: If the open glass cells are used and a certain number of cc of solution are pipetted off, then the color of this layer should be matched by a 2 cm layer of ulmin solution of concentration $\frac{1}{4}$, as the solution must be light enough to permit readings through the blue screen where the transmittancy $\mathbf{T}$ is lowest. Concentration $\frac{1}{2}$ would be better for the red and green screens. However, since the thickness, b, is not known, $-\log \mathbf{t}$ can not be calculated. On the other hand, if the usual parallel-sided photometer cells of known thickness are employed then that depth of color should be chosen for the red and green screens which is matched by 2 cm of an ulmin solution of concentration $\frac{1}{2}$. The thickness of the photometer cell chosen for the red and green screens should be such as to permit a reduction in the thickness for the blue screen. These niceties in adjustment are by no means superfluous, as the effective wave length of the color screen changes with a change in color intensity of the solution, since the solution itself acts as an additional light

filter. Therefore, it is necessary always to use solutions of nearly the same depth of color by so choosing the thickness of cell and color concentration of the solution that the color of the solution, when viewed through the cell, approximately matches that of the specified thickness of ulmin solution of the required concentration. The only exception is made if very light-colored solutions are investigated.

If a spectrophotometer is used, a solution whose color is equivalent to ulmin concentration 1 for $b=2$ cm is used for the range between the red and wave length 500 mμ. Concentration ½ then indicates the range of color concentration from 500 mμ to the blue-violet, wave length 436 mμ. If necessary, thickness, b, of the colored sugar solution is reduced to $b=1$ cm, or $b=0.50$ cm, the concentration, $c=0.7$ g d.s./1 cc, being maintained at all times.

III. STANDARDIZED PROCESS OF COLORIMETRIC CLARIFICATION

1. PREPARATION OF TURBID SOLUTIONS WITH WATER AS A SOLVENT

Boiling-hot water is added very slowly to the sugar product under constant rapid stirring, paying no attention to the color. The slow addition of water at boiling temperature is for the purpose of maintaining the degree of dispersion of colloidal nonsugar which otherwise is apt to coagulate. Such coagulation always occurs sooner or later in diluted solutions and causes a turbidity which will remain after filtration, so that the solution appears more or less turbid in the dark-room test, even though it may appear perfectly transparent in diffuse daylight. Enough water is added in the manner described to produce a density close to 55° Brix; that is, 55 g of dry substance per 100 g of solution. As photometric analyses are to be made, it is essential that the concentration be expressed in terms compatible with the fundamental laws of photometry. The term, Brix—that is, per cent dry substance by weight which is commonly used—does not fulfill this condition. It is essential to define the concentration as grams colored dry substance per cc, the desired concentration, c, being always approximately 0.7 g dry substance per 1 cc. A sugar solution of 55 Brix contains approximately 0.7 g dry substance per 1 cc (that is, 55 Brix times true density = 0.7 g per cc). The sugar product is weighed off and transferred to a volumetric flask if cross checks are desired; otherwise the product may be dissolved in an open beaker. The latter course is permissible in routine analyses if the dry substance content is determined by refractometer. It is not recommended in precision analyses that a common Brix spindle or Westphal balance be used.

The solution is finally cooled under the tap and adjusted to the required weight or volume to give a concentration of approximately

0.7 g per 1 cc. Turbidity is in many cases due merely to the haphazard, indifferent method of preparing solutions without attention to the details described. It is, however, only occasionally that the above procedure fails to give a satisfactory solution. Occasionally it may be necessary to repeat the process of preliminary clarification and filtration.

Should cold or lukewarm water be used, or too much water be added at once, so that a dilute solution is produced locally before stirring brings equilibrium, the solutions may contrast sharply with carefully prepared solutions from the same sugar. The magnitude of the reaction on the transparency will depend in some degree upon the character of the nonsugar in the sugar product. The observed differences in the absorption of such filtrates show great variation, the magnitude changing with time, temperature, concentration, and the mode of preparation. A product and its solution may be very light colored and yet show greater variations in absorption through faulty preparation than are found in much darker colored solutions under like conditions. Turbidity, ordinarily overlooked in colorimetric clarification, is a most common and aggravating source of error in the estimation of absorption, and hence ultimately of color. Such errors are eliminated only by the careful preparation of the original turbid solution of approximately 0.7 g d. s./1 cc.

After the turbid solution has been made up all floating material, sediment, etc., not chemically related to the saccharine dry substance should be removed by a preliminary straining or filtering through linen or cotton cloth or fine screens. The first run should be discarded as a precautionary measure, as is customary in all polarimetric determinations.

2. DILUTION OF COLOR BY A CONCENTRATED DILUENT

A dilution of color is necessary if the turbid solution prepared as above, when placed in a photometer cell usually 2 cm in thickness, is so dark colored that good photometric readings can not be made. This dilution is always accomplished by the addition of the concentrated colorless sucrose solution, whose preparation has been described on page 274.

Water is never used as a diluent of color and is used only as a solvent of the saccharine dry substance in the preparation of the turbid solutions. By the use of the concentrated diluent the coloring matter in the turbid solution is diluted to an appropriate degree and the dry substance concentration maintained. Precipitation of colloidal matter is thus prevented and a satisfactory filtrate obtained. The turbidity in the solutions before filtration must be stable. This means that the solutions must have that particle concentration of colloidal matter per unit volume which obtains naturally at the given

temperature and concentration and which, therefore, remains unchanged during the analytical preparation and observation. If water is used as a diluent of color, there is initiated a process of coagulation and sedimentation which may continue for a long period of time and which is uninterrupted by any process of filtration. It has been observed in such solutions that the degree of transparency may gradually change during the short time required for making the photometric observations. Occasionally a distinct haze will remain in the solution, even after careful preparation and filtration through asbestos. This is especially true in the case of residual massecuites, run-offs, and molasses.

Occasionally the slow and careful addition of boiling-hot water to residual sugar products of the type mentioned above may cause unstable turbidity, even though the final solution has a concentration of approximately 0.7 g d. s./1 cc. In such cases water as a solvent may advantageously be replaced by a diluent whose dry substance content may vary between 40 and 50 per cent sucrose by weight, depending in part upon the required degree of dilution of color. The resulting turbidity may be successfully removed by filtration through the final asbestos pads. Numerous observations on a number of different types of residual sugar products are necessary to obtain the data to determine the correct mode of procedure in such cases. It is interesting to note that sucrose here may be said to act as a protective colloid. Concentrated solutions of sucrose are considered to be near the border line of the crystalloidal and colloidal state of matter. At present it must suffice to call attention to the necessity for further study of such conditions which lead to variations in the methods of analytical preparation, and thus to different magnitudes of the negative logarithms which measure the absorbed light.

Because of the wide range of color intensities in technical products, the thickness, b, of the cells may vary between 50 and 0.1 cm, and the rate of dilution of color may vary between 1 and 50 for thickness $b=2$ cm. The appropriate degree of saturation of color in the mixed solution is chosen preferably for a cell-thickness $b=2$ cm, and not less than 1 cm.[6] Absorption may then be observed for that concentration in the red end of the spectrum between 700 mμ and 500 mμ. A reduction of thickness, b, to 0.5 cm in the blue end of the spectrum is necessary and should invariably be made in preference to any additional dilution of color. The use of a cell with $b=1$ cm for observations in the red end of the spectrum generally requires a dilution of color beyond 480 mμ, as $b=0.5$ cm is then still too great to permit accurate observation. The choice of the appropriate degree

[6] An assortment of plane parallel cells of different thicknesses; that is, cells of 20, 10, 5, 2, 1, and 0.5 cm may very materially shorten the process of preparing the solutions by permitting the elimination of one or more dilutions which would otherwise be necessary for the blue end of the spectrum.

of saturation of color is facilitated by the comparison of the colored solution with the ulmin solution of proper concentration, for $b = 2$ cm, as described on page 275. Smaller thicknesses than $b = 3$ mm are not recommended unless the cell is so constructed as to permit easy cleaning.

Whatever the choice in methods of color dilution, whether on the basis of volume or weight, the resultant mixed solution, consisting of a colored solution and a colorless diluent, will always be turbid and therefore require filtration.

3. CLASSIFICATION OF FILTRATES AND THE PRELIMINARY CLARIFICATION

So far there has been described the process of preparing the original turbid solution and the method of securing the desired and appropriate degree of color concentration and at the same time the correct dry substance concentration. This turbid mixture or the original turbid solution is to be filtered and thereby changed into a transparent filtrate. Thus far the original turbid solution has been subjected only to a simple straining process for the removal of material foreign to the saccharine dry substance (for instance, bagacillo).

If this turbid solution is of a sufficiently good quality, it may at once be filtered through the final asbestos pads to produce the final optical filtrate. In most cases, however, especially in the case of impure, colored products, or of products obtained in the laboratory by special treatments in decolorizing and purification processes, the physical condition of the solution is such that a preliminary clarification is necessary before sending the solution to the final filtering pads. This preliminary clarification is accomplished by shaking the impure solution with asbestos fiber and filtering through a Gooch crucible. If the liquors contain sediments of various kinds—for instance, from storage tanks or from carbon treatments—the greater portion of it may be removed by centrifuging, using filter cloth over the centrifuge screen.

Approximately 100 g of the turbid solution is shaken for 5 to 15 minutes with about 2 g of dry optically clean asbestos fiber. Dry asbestos is used to avoid any dilution of the turbid solution. The mixture of loose asbestos fiber and impure liquor is poured, a little at a time, into an empty Gooch crucible. Slight suction is first applied, so that a fine layer of asbestos appears at the bottom of the crucible. A little more is poured in and the operation is repeated several times. As the layer of asbestos gets thicker greater suction may be applied.

The first rather cloudy portions of filtrate are returned to the pad to be refiltered. The pad itself is built up during the process of filtration and constantly increases in thickness and efficiency. Care-

ful handling of this process of filtration will make it possible to obtain a clear filtrate by a single filtration. The filtrate is a clear solution suitable for quantitative chemical analysis, but not for purposes of optical analysis. It is ready, however, to be at once filtered through the final asbestos pads.

The process of preliminary clarification will produce a greater volume of filtrate in a given time than would be obtained in the process ordinarily used. It has been customary to pour the murky liquor upon a previously prepared pad, or a layer of filter paper in a Büchner funnel. Such a procedure may lead to complete failure, especially in the case of low-grade technical liquors or the raw wash from affining processes of raw sugars entering the refining process. With these liquors a slimy film will, within a very few minutes, make filtration impossible. This is especially important in case carbon liquors are to be separated quickly while still hot[7] from the carbon at the end of a certain period of digestion.

No effort is made to maintain a high temperature while filtering the solution through the final pads; in fact, it is preferable to filter at room temperature. It is advisable that each operator study the optical effects of variation in the preparation of transparent solutions. Occasionally less rigorous methods of preparation may be used; for instance, the use of 0.5 or 1 g of asbestos instead of 2 g in the preliminary clarification.

4. FINAL FILTRATE

(*a*) PREPARATION

The final process in producing a solution of a quality suitable for optical analysis is the filtration through the final asbestos pads whose preparation has been described on page 271. This filtrate is called the final filtrate.

The solutions which go to these pads are fairly transparent, yet too turbid for optical analysis. They range in turbidity from the brilliant filtrates of technical liquors, as produced in the factory or the refinery or by the preliminary clarification described above, to liquors whose turbidity is such that a preliminary clarification is barely avoided.

Ordinarily from one to six crucibles or filtering units may be handled by one operator. When starting the filtration, each asbestos pad is moistened with a few drops of water. This is followed by a rinsing process with a few cc of the turbid solution to be filtered. The rinsing should be repeated a few times, each time barely covering the pad. A quicker filtration is obtained in this manner than if the turbid

[7] The greater part of the carbon is removed from the hot liquor by centrifuging, using a cotton filter cloth inside the screen lining. The murky run-off goes to the preliminary process of clarification. Stammer recommended a cooling off of the mixture before separation.

solution is at once poured upon the dry asbestos pad. As soon as the pads have been sufficiently rinsed the receptacle containing the rinsings is removed and replaced by a clean, dry receptacle. The rate of filtration should be such that the filtrate comes through and falls into the bottle drop by drop. The vacuum should be regulated so that the rate of flow never increases to the point where a steady stream is produced. The pads should be kept covered with liquid during a filtration. Although all the filtering units have been prepared to filter alike on the same grade of liquor, the rate will vary with the viscosity of the different samples. As soon as the required amount of a filtrate has collected in one of the receiving bottles that unit is cut out without disturbing the others and the filtrate poured into a clean, dry receptacle and again filtered through the same pad. It is advisable to study the optical effects of 2 to 6 filtrations; 2 to 4 complete filtrations ordinarily are sufficient.

All filtrations through asbestos should be so conducted as to entail the least loss by evaporation, thus minimizing the consequent change in the concentration of the solution.

The amount of loss by evaporation depends somewhat upon the temperature at which the filtration is made. In some cases, even at room temperature, a change of as much as 0.25 per cent dry substance concentration may occur. Such a change is of more importance in the case of dark colored solutions which require a rather large dilution than in the case of lighter colored products. It is advisable to have a check upon all such sources of possible error by taking refractometer readings before and after filtration.

In routine methods of calculating color such changes are ignored, the concentration of the solution which goes to the photometer for analysis being assumed to be the same as that of the turbid solution before filtration. However, in precision work these small changes are taken into account by basing the concentration upon refractometer and density measurements of the final filtrate.

The volume of the filtrate required in most cases is small, ranging from a few cubic centimeters only for the dark colored solutions which require the use of the smaller cells (2, 1, and 0.5 cm thickness) to about 250 cc for very light colored solutions which require the use of the larger cells (20 cm or more in thickness).

If the pads are used a number of times after washing and rejuvenating them, it is advisable always to use a particular pad for the same grade of liquor. A light-colored solution should never be filtered through a pad that has been used for darker colored solutions, such as soft sugar No. 15 or molasses. It will be found instructive to study the behavior of pads which have become loaded with colloidal matter by filtering a portion of the solution through a pad that

has been used several times and another portion of the same solution through a new pad. If the filtrates are examined in the dark room, as described below, surprising differences will be observed, even though the used pad was seemingly quite thoroughly washed out. It is because of such possible effects that a new pad for each solution to be filtered is recommended, and that the optical effect of variation in preparation should be known by special study, if necessary.

(*b*) EXAMINATION OF TRANSPARENCY

The final filtrates should never be examined in diffuse daylight nor in common round vessels, except, perhaps, as a rough preliminary step.

An examination of every final filtrate should be made in the dark room by passing an intense and nearly parallel beam of light through the photometer cell containing the solution. The solution may be examined from any direction except in a direct line with the beam of light. The effect observed is somewhat similar to the Tyndall phenomenon. The path of the beam of light through the solution can easily be seen by means of the light reflected by floating particles in exactly the same way that the path of a beam of sunlight shining through a window can be seen by means of the light reflected by dust particles in the room.

In the present investigation a suitable light beam was obtained from a white lined box containing two 350-watt stereoptican lamps which served as the light source for the spectrophotometer. The side opposite the openings was covered by a plate of plaster of Paris which had been smoked with magnesium oxide to increase its diffuse reflecting power, the light utilized being that reflected by this white surface and not that coming directly from the lamp filament.

If a solution is held in front of one of the openings in the light box and examined under the conditions stated above, suitable transparency or lack of it is clearly revealed. Filter-paper filtrates, whose transparency would be considered perfectly satisfactory if examined by diffuse daylight, show any degree of turbidity from a slight haze to almost opaqueness, resembling an emulsion or heavy fog.

Surprising differences in transparency will be observed for solutions of the same substance due to differences in preparation. This is true for all of the many different technical sugar products, regardless of the quality of the product.

No physical constant which quantitatively measures the degree of transparency has so far been utilized. However, the above simple method of examination in the dark room without a Tyndallmeter or other similar instrument appears to be satisfactory.

(c) GENERAL OBSERVATIONS

In the present investigation several clarifying agents were studied besides asbestos, such as kieselguhr, talcum, magnesium carbonate, and filter-paper pulp, as well as certain grades of chemical filter paper. The detailed results obtained will be reported in a subsequent publication. No selective adsorption was found for filter paper, filter-paper pulp, or asbestos, and only a very slight amount for solutions clarified by talcum. Magnesium carbonate and kieselguhr, on the other hand, affect the coloring matter selectively, so that the tints of the filtrates differed materially. Besides ultrafiltration, asbestos filtration of concentrated solutions alone gave satisfactory transparent solutions. Existing analytical routine practice in colorimetric clarification, as developed in 1860, has therefore been discarded. The new viewpoints which govern the preparation of solutions of technical sugar products in the present attempt to standardize the process of colorimetric clarification are in the main based upon the study of advances made in the chemistry of colloids since the discovery of the Tyndall phenomenon and the invention of the ultramicroscope. The analytical proofs for the necessity of improving transparency by simple filtration methods will be presented in a later publication. The records presented at the close of this paper (Table 1) concern merely the differences in absorption for filter-paper filtrates of dilute solutions, as opposed to asbestos filtrates of concentrated solutions.

IV. PHOTOMETRIC OBSERVATIONS AND THE CALCULATION OF RESULTS TO A UNIT BASIS

1. SPECIFIC ABSORPTIVE INDEX, $-\log t$

After a suitably transparent solution has been prepared with a correct dry substance concentration and a suitable color concentration a parallel-sided cell of suitable thickness is filled and placed in one beam of a photometer. An exactly similar cell filled with distilled water or with a colorless sucrose solution is placed in the comparison beam in order to compensate for losses by reflection at the cell surfaces and eliminate corrections for this effect. A spectrophotometer, a simplified spectrophotometer, or other color measuring device which is capable of measuring transmittancy for monochromatic light of wave length 560 mμ, or for a narrow band of the spectrum whose effective wave length is 560 mμ, may be utilized. For routine work the mercury arc with color screens may be used as the light source in connention with a simplified spectrophotometer. Measurements of $\mathbf{T}$, or $-\log \mathbf{T}$, are made for the green line, 546 mμ, and the yellow lines, 578 mμ. The reading for 560 mμ is then ob-

tained by a process of interpolation between the readings for the first two wave lengths or, better, by applying a properly determined correction factor to one of them.[8]

The transmittancy measurement $\mathbf{T}$ [9] determined for the concentration, c, and thickness, b, is reduced to unit basis, as regards concentration and thickness, by means of the equation $\mathbf{t}=\sqrt[cb]{\mathbf{T}}$, or $-\log \mathbf{t}=\frac{-\log \mathbf{T}}{cb}$, which expresses Lambert's-Beer's law. It is to be noted that the photometer scale may be graduated in terms of $\mathbf{T}$ (transmittancy), or directly in $-\log \mathbf{T}$, the latter direct reading eliminating one step in the calculation. The thickness, b, for any cell is a constant, and c is readily calculated, utilizing for this purpose the refractometric and density measurements.

In all cases, whether or not the colored solution has been diluted, the concentration, c, is expressed as grams of original colored dry substance per 1 cc of the final solution upon which the transmittancy measurement is made. The concentration of the diluent is designated by c_D and likewise the total concentration of the mixture—that is, colored dry substances plus diluent dry substance—by C_M. In the simple case where no dilution of color is necessary, c obviously is obtained by multiplying together the refractometer per cent dry substance, R (d. s.), and the density, and dividing by 100. Thus, $c=\frac{R\text{ (d. s.)}\times d}{100}=$grams of colored dry substance per 1 cc of solution.

In the case where dilution of color becomes necessary—for instance, for 436 mμ of No. 15 sugar—c may readily be calculated from the refractometer and density measurements, together with the relative proportion of colored solution and diluent used to prepare the final solution. The calculations may be made in various ways according to the experimental procedure in making up the mixture and according to the degree of precision required. Several different methods are given below. They are intended to cover the variations in procedure which are sometimes forced upon the operator either by the character of the sugar products or by the limited amount of equipment available.

In the following calculations examples 1 and 2 illustrate the methods for the simple cases where the concentrated diluent is assumed to be colorless. The case where it is not colorless is illustrated in example 2(*a*).

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[8] Deduct 48 per cent of the difference between $-\log \mathbf{t}$ at λ546 and λ573 from $-\log \mathbf{t}$ at λ546; the result is $-\log \mathbf{t}$ at λ560.

[9] The transmittancy T of a solution is obtained by conversion of the actually observed scale reading of the photometric device, the conversion factor varying with the type of instrument. The transmittancy T is always the transmitted fraction of the incident light. See "Color nomenclature in the sugar industry" immediately preceding.

2. METHOD A—VOLUME BASIS

EXAMPLE 1.—If a turbid solution of a colored sugar product has a refractometer Brix of 55.0 and a density of 1.258, the d. s. concentration of this turbid solution is $\frac{55.0 \times 1.258}{100} = 0.6916$ g per 1 cc. Suppose it is found necessary to dilute color by adding colorless diluent in the proportion of about four volumes of diluent to one volume of turbid solution. This dilution may be carried out in either of two ways:

(*a*) About 20 cc of the turbid solution may be placed in a 100 cc flask and weighed. Suppose the weight of the solution is found to be 25.130 g in air with brass weights. The flask is then filled to the mark with concentrated diluent, the final adjustment of the volume being made at 20° C. The concentration of the original colored d. s. in the final solution, therefore, is $c = \frac{25.130 \times 55.0}{100} = 0.13821$ g in air with brass weights. When this value is reduced to vacuo,[10] c becomes 0.13832 g per cc This is the value to be used in the equation expressing Lambert's-Beer's law.

(*b*) The two solutions which should be at the same temperature (near 20° C.) may be pipetted off into a beaker with pipettes which are standardized to contain a definite volume. In this case care must be exercised to thoroughly rinse both pipettes with the solution after mixing in order that the solution adhering to both pipettes may be of exactly the same concentration as the mixture in the beaker. Suppose exactly 20 cc of the above turbid solution containing 0.6916 g d. s. per 1 cc is mixed with 80 cc of diluent. The concentration of colored dry substance will have been reduced to one-fifth of its previous value. Therefore, $c = \frac{0.6916}{5} = 0.13832$ g colored dry substance per 1 cc in vacuo.

Another way of making the same calculation is as follows: 20 cc of the solution containing 0.6916 g colored dry substance per 1 cc will contain $20 \times 0.6916 = 13.832$ g of colored dry substance. When this solution is diluted with 80 cc of diluent, the total volume is 100 cc. Since 13.832 g of colored dry substance is contained in this 100 cc of mixed solution, $c = \frac{13.832}{100} = 0.13832$ g colored dry substance per 1 cc as above.

It will be observed that in both (*a*) and (*b*) the concentration, (*c*), has been that of the original turbid mixture before filtration. In

[10] In order to be consistent, all concentrations throughout this paper have been reduced to vacuo. The density tables (Plato's) ordinarily used in sugar work refer to densities in vacuo. While it would be inconsistent to use these tables in connection with weighings in air with brass weights, in most cases in industrial laboratories the error caused by so doing is entirely negligible.

these cases it is assumed that the concentration of the colored dry substance in the final filtrate is the same as in the turbid mixture. This is not strictly true and is taken into account in the more precise but somewhat longer method of calculation given below. Even in routine analyses it is advisable to check this point frequently by making refractometer readings before and after filtration, both for the purpose of knowing how great an error the above assumption is causing and also for the purpose of controlling this error by so arranging the conditions under which the filtration is carried out that the differences in refractometer readings before and after will be as small as possible.

3. METHOD B.—DILUTION OF COLOR ON A WEIGHT BASIS

EXAMPLE 2.—The solutions are the same as in example 1. The original turbid solution has a refractometer Brix of 55.0, the diluent a refractometer Brix of 51.0, and the turbid mixture a refractometer Brix before filtration of 51.81 and after filtration of 52.0. The true density of the turbid mixture after filtration was 1.2406.

Suppose 12.565 g (10 cc) of the original turbid solution is weighed out and mixed with 49.362 g (40 cc) of colorless diluent. The weight of the colored dry substance used is 55 per cent of 12.565 or 6.9109 g. The weight of diluent dry substance used is 51 per cent of 49.362 or 25.1746 g.

The proportion of colored dry substance in the total dry substance of the turbid mixture is therefore $\frac{6.9108}{6.9109+25.1746}$, or 21.54 per cent, and the proportion of diluent dry substance is 78.46 per cent.

For all practical purposes the weight of colored dry substance in relation to the weight of the total dry substance remains unchanged during filtration, the increase in concentration during filtration being due to evaporation. The total dry substance concentration of the final filtrate is $\frac{52.0\times 1.2406}{100}=0.64513$ g per cc in vacuo, 21.54 per cent of which is original colored dry substance and the rest diluent dry substance.

Therefore, $c=21.54$ per cent of $0.64513=0.13896$ g of original colored dry substance per 1 cc of the final filtrate. This is the value of c to be used in reducing the photometric readings to unit basis by means of Lambert's-Beer's law. Attention is here directed to the fact that in this method the concentration, c, is that of the final filtrate and not that of the solution before filtration. If the concentration of the turbid mixture had been used instead of that of the final filtrate, the value of c would have been the same as that obtained in example 1.

In both of the above examples the same final filtrate was read on the photometer in a 2-cm cell. The transmittancy for the wave length 560 mμ was $\mathbf{T}=75.0$ per cent or 0.75, and at wave length 436 mμ (mercury blue), $\mathbf{T}=32$ per cent or 0.32. From reference to a table of logarithms

$-\log \mathbf{T}=0.1249$ for 560 mμ and 0.4949 for 436 mμ.

$b=2$ cm

$c=0.13832$ g per cc if the approximate method of calculation is used as in examples 1 (a) and 1 (b), and

$c=0.13896$ g per 1 cc if the longer but more accurate method of example 2 is used. Putting these value in the equation

$$-\log \mathbf{t}=-\frac{1}{cb}\log \mathbf{T}$$

we have

(example 1) $$-\log \mathbf{t}_{\lambda=560}=\frac{1}{0.13832\times 2}\times 0.1249=0.4515,$$

(example 2) $$-\log \mathbf{t}_{\lambda=560}=\frac{1}{0.13896\times 2}\times 0.1249=0.4494,$$

$$-\log \mathbf{t}_{\lambda=436}=\frac{1}{0.13896\times 2}\times 0.4949=1.781.$$

Whenever more than one photometric reading is made for the same solution in the same cell it is advantageous to calculate $\frac{1}{cb}$ and then multiply this value by each of the negative logs. The two examples show the difference that may be expected between the approximate method and the longer but more accurate one.

Example 2 (a).—This example is calculated by the same method as example 2, except that the slight absorption by the diluent in the blue end of the spectrum is taken into account. It is given both to illustrate the method of calculation and to show about how much the absorption of a practically colorless diluent may be expected to affect the recorded measurements.

The $-\log \mathbf{T}$ for 436 mμ, recorded above in example 2, is here designated as $-\log \mathbf{T}_M$. It is the transmittancy for the mixture as measured and is made up of two parts, the $-\log \mathbf{T}$ of the colored sugar solution of d. s. concentration, c, and the $-\log \mathbf{T}_D$ of the diluent of d. s. concentration, c_D; that is,

$$-\log \mathbf{T}=(-\log \mathbf{T}_M)-(-\log \mathbf{T}_D)$$

The value of $-\log \mathbf{T}_D$ may be calculated by Lambert's-Beer's law if we know the concentration, c_D, of the diluent d. s. in the mixed solution and its specific absorptive index, $-\log \mathbf{t}_D$. The absorption of the pure diluent will be assumed to have been measured in a cell

not less than 20 cm, taking all other necessary precautions to insure accurate results, and its $-\log \mathbf{t}_D$ at $\lambda = 436$ mμ found to be 0.0096. Since the d. s. concentration of the mixture (example 2) is 0.64513 g per cc, 78.46 per cent of which is diluent d. s., $c_D = 0.50617$ g per cc.

$$-\log \mathbf{T}_D = c_D b\ (-\log \mathbf{t}_D) = 0.50617 \times 2 \times 0.0096 = 0.0097.$$

Therefore

$$-\log \mathbf{T} = 0.4949 - 0.0097 = 0.4852.$$

Since

$$-\log \mathbf{t} = \frac{1}{cb}\ (-\log \mathbf{T}),$$

$$-\log \mathbf{t}_{\lambda=436} = \frac{1}{(0.13896 \times 2)} \times 0.4852 = 1.746.$$

as against 1.781 by the method of example 2. The difference is less than 2 per cent even for the extreme blue where the absorption is the greatest.

Example 3.—In case the Brix (per cent dry substance by weight) of a heavily colored product is unknown or is only known approximately, for example, through daily averages of routine analyses, the original Brix may be calculated from the known rate of dilution, r, the Brix of the diluent, and the Brix of the total dry substance in the mixture by means of the formula

$$\text{Brix} = r \cdot \text{Brix}_M - (r-1)\ \text{Brix}_D$$

This method is as exact as the direct refractometric observation of a special solution which is made up by dissolving 1 part of the product in 1 part of water and doubling the Brix value of the converted refractive index actually observed. In the above equation

$$r = \frac{\text{Weight of diluent} + \text{weight of colored solution}}{\text{Weight of colored solution}}$$

For instance, suppose $r = \frac{9+1}{1} = 10$ parts by weight of tubrid mixture to 1 part of colored product; Brix of turbid mixture = 54.6 and Brix of diluent = 50.2. Therefore, $\text{Brix}_c = (10 \times 54.6) - (9 \times 50.2) = 94.2$ per cent. From this point on the procedure is that given in example 2 above.

Example 4.—Calculation of the Brix_D, of the colorless diluent required to produce the desired Brix_M, of the turbid mixture when a definite and particular rate of color dilution is desirable, as when the method illustrated by example 3 is applied. Suppose the Brix_c of the original colored product is known approximately to be about 98, that the concentration of the turbid mixture is to be about 54 Brix_M, and that the rate of dilution, $r = 5$, produces a turbid mixture of

desirable color concentration. The required Brix_D of the less concentrated diluent may be calculated from the formula

$$\text{Brix}_D = \frac{(r \cdot \text{Brix}_M) - \text{Brix}_c}{r-1}.$$

Substituting the above values in this equation

$$\text{Brix}_D = \frac{(5 \times 54) - 98}{(5-1)} = 43.0$$

In all cases where possible the concentration c, should be based upon refractometer dry substance, which is the most simple and accurate method of determining dry substance by weight.

V. SUMMARY OF THE METHOD OF PROCEDURE

1. Make up a 55 Brix sugar solution, as described on page 276.
2. Determine the per cent d. s. by refractometer and the density (the latter either by table or by experiment as required by the grade of the product).
3. Observe whether this turbid solution appears to be of a suitable color concentration.
4. (*a*) If so, complete the process of filtration either by filtering directly through the final pads or by first applying the process of preliminary clarification as required by the quality of the solution.
4. (*b*) If not, the color must be diluted while maintaining unchanged the total dry substance concentration. This may be done by the method described. Complete the filtration as under 4(*a*).
5. Fill a parallel-sided cell of suitable thickness and read on a spectrophotometer, a simplified spectrophotometer, or other color measuring device, capable of measuring transmittancy for monochromatic light of wave length 560 mμ, or a narrow band of the spectrum whose effective wave length is 560 mμ.
6. Record (for routine technical analysis) (method 1):
(*a*) The refractometer d. s. of the turbid solution.
(*b*) Density of the turbid solution (unless dilution of color is necessary).
(*c*) If dilution is made, record also the volume (or weight) of the colored solution used, and
(*d*) Either the volume (or weight) of the diluent used or the total volume of the colored solution and the diluent. If the more precise method (method 2) is used, record:
(*a*) Refractometer d. s. of the turbid solution. Refractometer d. s. of the colorless diluent.
(*c*) Weight of each used.
(*e*) Refractometer d. s. of final filtrate.

(*f*) Density of final filtrate.

In all cases record also:

(*g*) Thickness of the cell used.

(*h*) Wave length of light.

(*i*) Photometric reading obtained.

7. Reduce the reading obtained to unit basis as regards concentration and thickness by calculating the specific absorptive index, $-\log \mathbf{t}$, from the equation, $-\log \mathbf{t}=\frac{1}{cb}(-\log \mathbf{T})$. The concentration of coloring matter itself remains unknown.

8. In order to reduce the $-\log \mathbf{t}$ at 560 mμ to n units of coloring matter (equivalent to n sugar color degrees) divide it by the absorption unit, $-\log \mathbf{t}_1$, of the standard at the same wave length. This value for the provisional standard adopted is 0.00485 at $\lambda=560$ mμ for all types of coloring matter. One absorption unit at $\lambda=560$ mμ, and also at all other wave lengths, is equivalent to one unit of coloring matter which evokes a color sensation of one color degree. The value, n absorption units, represents the sum total effect of absorption at all wave lengths. It is therefore a measure of n units of coloring matter in 1 g of saccharine dry substance and is the final value to be recorded as characteristic of the sample measured. The spectrophotometric basis for the derivation of these units will be presented in a subsequent publication.

VI. OPTICAL EFFECT OF DIFFERENT METHODS OF CLARIFICATION

In all cases additional measurements at other wave lengths than 560 mμ, especially the shorter wave lengths (for example, the Hg lines 546 mμ and 436 mμ), may be made to yield valuable information as to the efficacy of various processes of manufacture, especially when studied as absorption ratios, Q. This phase of the problem is dealt with in the following discussion of the optical effect of different methods of colorimetric clarification.

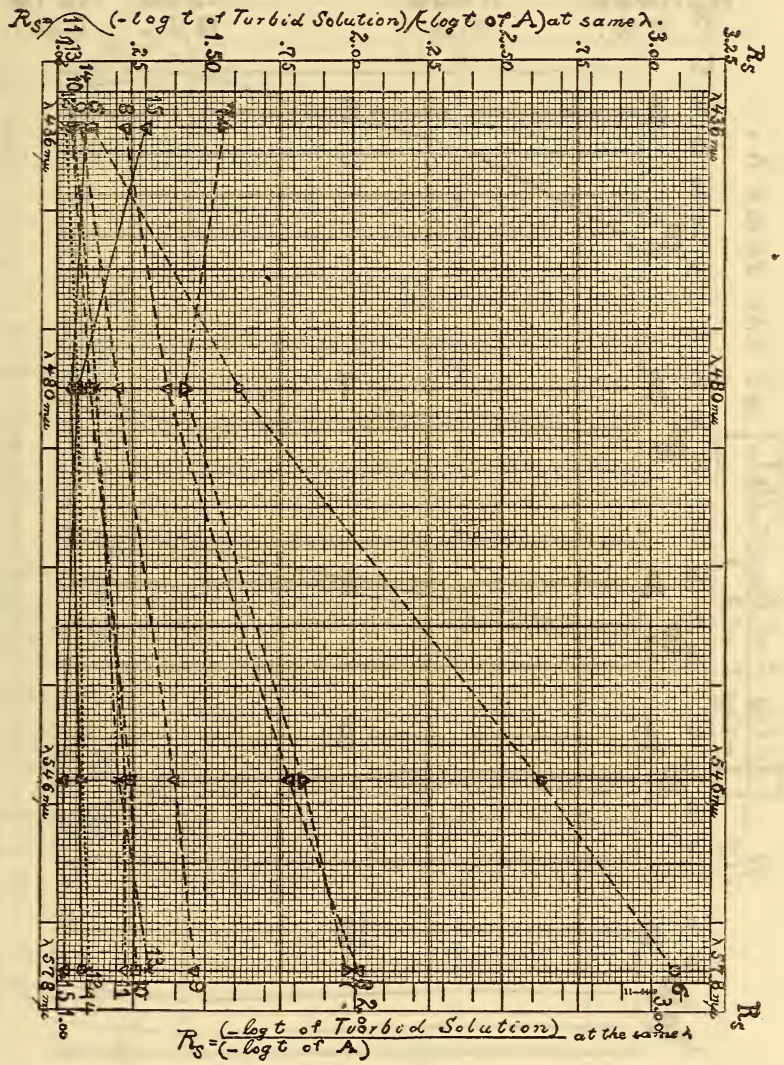

FIG. 2.—*A graphic comparison of solutions of the same type before and after clarification and filtration (Table 1, columns 8 to 11)*

The ratios, R_s, between the final asbestos filtrate, *A*, and the turbid solution from which it was obtained

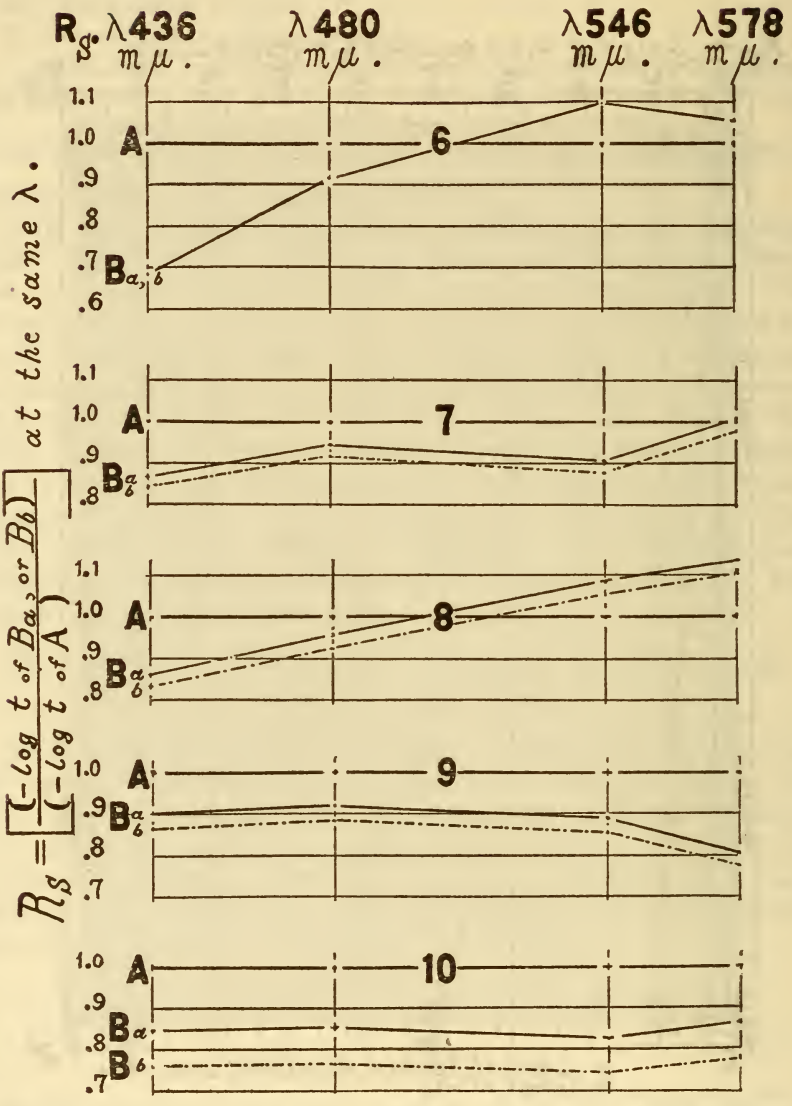

FIG. 3.—*A graphic comparison of intensity ratios of two different types of solutions (Table 1, columns 8 to 11)*

A, the final asbestos filtrate,
B, the dilute kieselguhr-filtrate through filter paper

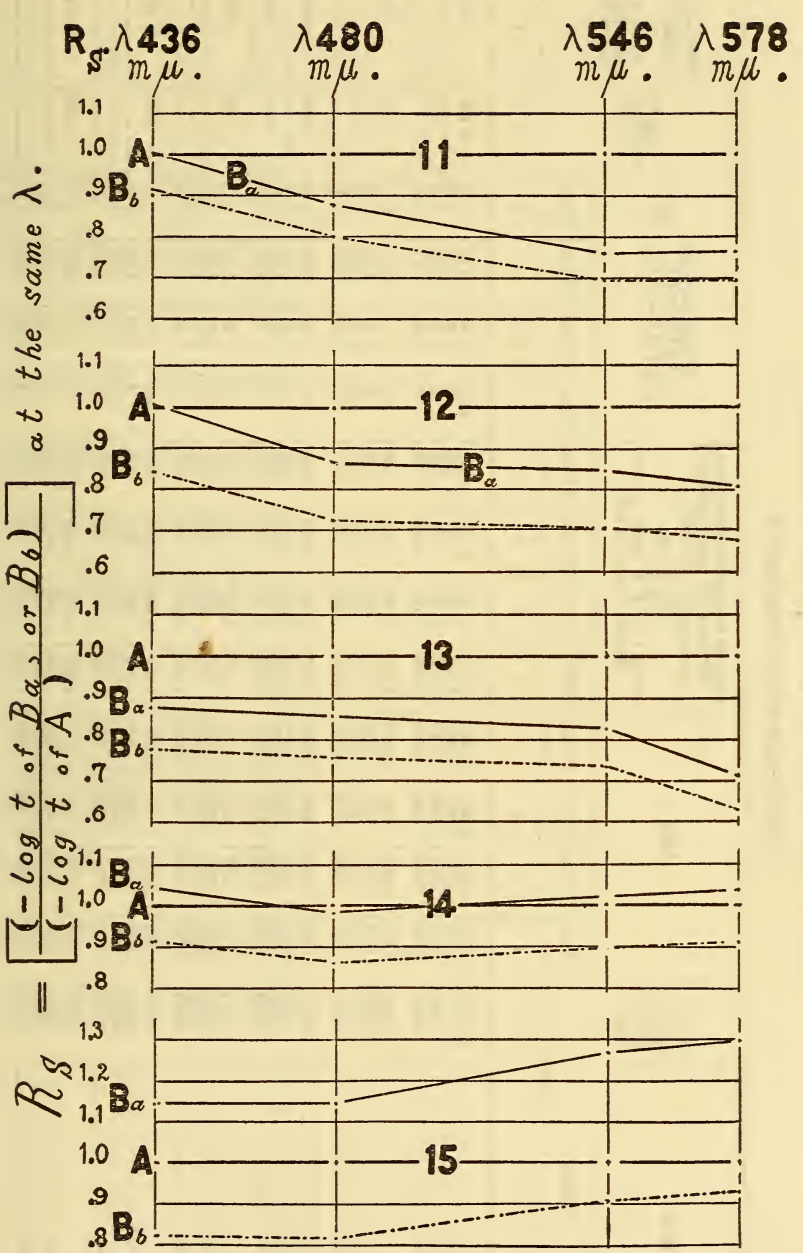

FIG. 3.—*A graphic comparison of intensity ratios of two different types of solutions (Table 1, columns 8 to 11)*

A, the final asbestos filtrate,
B, the dilute kieselguhr-filtrate through filter paper

TABLE 1.—*Optical effect of different methods of clarification*

[A typical series of absorption measurements]

Sugar	Solution	Concentration, c, (g d. s. /cc)	−log t				Ratio of the specific absorptive indexes of two sugar solutions at the same wave length $\frac{-\log t}{-\log t_A}=R_s$ (−log t of A is taken as the standard equal to 1.00)				Absorption ratio: $\frac{(-\log t \text{ at any } \lambda)}{(-\log t \text{ at } \lambda=546\ m\mu)}=R_\lambda$				$-\log t_{\lambda=560\ m\mu}$	$\frac{-\log t_{\lambda=560}}{0.00485}=\frac{}{n}$ Units of coloring matter in 1 g d. s.
			578 mμ	546 mμ	480 mμ	436 mμ	578 mμ	546 mμ	480 mμ	436 mμ	578 mμ	546 mμ	480 mμ	436 mμ		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
No. 6	A	0.64972	0.0926	0.1435	0.400	1.0403	1.000	1.000	1.000	1.000	0.65	1.00	2.79	7.25	0.120	24.74
	B_a	.076	.0972	.1575	.3668	.7168	1.051	1.098	.917	.689	.62	1.00	2.33	4.55		
	B_b	.07604	.0971	.1574	.3666	.7164	1.050	1.097	.917	.689	.62	1.00	2.33	4.55		
	Turbid	.65279	.2848	.3782	.6449	1.1670	3.079	2.636	1.612	1.122	.75	1.00	1.71	3.09		
No. 7	A	.64972	.1419	.2013	.504	1.0513	1.000	1.000	1.000	1.000	.70	1.00	2.50	5.22	.175	36.08
	B_a	.05636	.1433	.1824	.4775	.9140	1.010	.906	.947	.869	.79	1.00	2.62	5.01		
	B_b	.05817	.1389	.1768	.4626	.8856	.979	.878	.918	.842	.79	1.00	2.62	5.01		
	Turbid	.65279	.2808	.3682	.7193	1.6441	1.979	1.829	1.427	1.564	.76	1.00	1.95	4.47		
No. 8	A	.64972	.1800	.2576	.6937	1.4657	1.000	1.000	1.000	1.000	.70	1.00	2.69	5.69	.212	43.7
	B_b	.04077	.2045	.2801	.6634	1.2614	1.136	1.087	.956	.861	.73	1.00	2.37	4.50		
	B_b	.04210	.1981	.2712	.6424	1.2216	1.101	1.053	.926	.833	.73	1.00	2.37	4.50		
	Turbid	.65279	.3633	.4592	.9525	1.8062	2.018	1.783	1.373	1.232	.79	1.00	2.08	3.93		
No. 9	A	.63979	.2731	.3929	.9815	1.860	1.000	1.000	1.000	1.000	.70	1.00	2.50	4.73	.34	70.1
	B_a	.02906	.2196	.3488	.9029	1.6757	.804	.888	.920	.901	.63	1.00	2.59	4.80		
	B_b	.03030	.2106	.3346	.8659	1.6071	.771	.852	.882	.864	.63	1.00	2.59	4.80		
	Turbid	.65279	.3989	.5492	1.1825	2.0101	1.461	1.398	1.205	1.081	.73	1.00	2.15	3.66		
No. 10	A	.65512	.2932	.4266	1.1171	2.099	1.000	1.000	1.000	1.000	.69	1.00	2.62	4.92	.364	75.05
	B_a	.02535	.2542	.3527	.9525	1.7814	.867	.827	.853	.849	.72	1.00	2.70	5.05		
	B_b	.02826	.2278	.3164	.8543	1.5978	.778	.742	.765	.761	.72	1.00	2.70	5.05		
	Turbid	.65279	.3732	.5303	1.2420	2.2159	1.273	1.243	1.112	1.056	.70	1.00	2.34	4.18		
No. 11	A	.65663	.5716	.7799	1.890	3.27	1.000	1.000	1.000	1.000	.73	1.00	2.42	4.19	.681	140.4
	B_a	.01548	.4352	.5919	1.6597	3.2789	.763	.759	.878	1.003	.74	1.00	2.80	5.54		
	B_b	.01708	.3974	.5394	1.5123	2.9877	.695	.692	.800	.914	.74	1.00	2.80	5.54		
	Turbid	.65279	.7023	.9550	2.1405	3.4592	1.229	1.225	1.133	1.058	.74	1.00	2.24	3.62		

No. 12	A	.65063	.6356	.9536	2.3111	4.1460	1.000	1.000	1.000	.72	1.00	2.42	4.35	.825	170.1		
	B_a	.01257	.5540	.8063	2.0024	4.1744	.808	.846	.866	.69	1.00	2.48	5.18				
	B_b	.01506	.4625	.6731	1.6716	3.4847	.675	.706	.723	.69	1.00	2.48	5.18				
	Turbid	.65279	.7573	1.0320	2.4723	4.2055	1.105	1.083	1.070	.73	1.00	2.39	4.13				
No. 13	A	.65512	.6571	.9032	2.2340	4.040	1.000	1.000	1.000	.73	1.00	2.47	4.47	.781	161.0		
	B_a	.01465	.4673	.7479	1.9125	3.5496	.711	.828	.856	.62	1.00	2.56	4.75				
	B_b	.01657	.4132	.6612	1.6909	3.1383	.629	.732	.757	.62	1.00	2.56	4.75				
	Turbid	.65279	.860	1.0888	2.5264	4.2055	1.309	1.206	1.131	.79	1.00	2.32	3.92				
No. 14	A	.65512	.9939	1.3372	3.1811	5.3342	1.000	1.000	1.000	.74	1.00	2.38	3.99	1.18	243.3		
	B_a	.00878	1.0337	1.3636	3.1272	5.5725	1.040	1.020	.983	.76	1.00	2.29	4.09				
	B_b	.01002	1.9058	1.1949	2.7402	4.8829	.911	.894	.861	.76	1.00	2.29	4.09				
	Turbid	.65279	1.0791	1.4381	3.3297	5.8522	1.086	1.075	1.047	.75	1.00	2.32	4.07				
No. 15	A	.65512	1.400	1.878	4.247	6.973	1.000	1.000	1.000	.75	1.00	2.26	3.71	1.646	339.4		
	B_a	.00682	1.8146	2.3738	4.8513	7.9879	1.296	1.264	1.142	.76	1.00	2.04	3.37				
	B_b	.00952	1.300	1.7005	3.4754	5.7224	.929	.905	.818	.76	1.00	2.04	3.37				
	Turbid	.65279	1.4381	1.9142	4.5449		1.027	1.019	1.070	.75	1.00	2.37					

1. EXPLANATION OF TABLE 1 AND FIGURES 2 AND 3

Table 1 gives the specific absorptive indexes ($-\log \mathbf{t}$) of 10 different soft sugars, the solutions being prepared (A) by the present method and (B) by the older method.

Column 1 gives the type number of the sugar.

Column 2 gives the type of solution. The solution marked "turbid" was the concentrated turbid solution made up according to the directions on page 276. Solution A was obtained from this solution by the process of clarification and filtration described on pages 279 and 280. Solution B was prepared by the older method.[11] The concentration of B was determined in two ways:

(*a*) From the weight of the soft sugar dry substance used and the volume of solution produced. The solution was made up in a volumetric flask, it being known from previous experiments what weight of any of the soft sugars would produce the definite volume of solution of the desired straw color. The dry substance content of the sugar by desiccation was also known.

(*b*) From the refractive index of the filtered solution and the density from Plato's table. It is to be noted that an accurate determination of dry substance by refractometer is difficult to make for these dilute solutions because of the relatively small change in the index with change in concentration.

Column 3 gives the concentration at which the photometric measurements of the transmittancies $\mathbf{T}$ were made. Except in the case of B_a the values of c were determined from the refractometer dry substance and density. In the case of the concentrated turbid solution the concentration was also determined from the known weight of dry substance in the commercial sugar weighed off and the known volume of solution produced. No differences were found between the concentrations obtained by the two different methods. In contrast to the close agreement between the two methods in the case of the concentrated solutions, it will be seen from Table 1 that in the case of dilute solutions the two methods give quite different results.

Columns 4, 5, 6, and 7 give the $-\log \mathbf{t}$ for different wave lengths; that is, the values obtained by reducing the observed $-\log \mathbf{T}$ to unit basis with regard to concentration and thickness by means of the formula

$$-\log \mathbf{t} = \frac{1}{cb}(-\log \mathbf{T})$$

It is to be noted that the transmittancy $\mathbf{T}$, thickness b, and $-\log$ transmittancy $\mathbf{T}$ are omitted.

Three different ratios in columns 8 to 11, 12 to 15, and 17 are discussed in detail below.

---

[11] The soft sugar was dissolved in sufficient water to give the usual straw-colored solution ordinarily used in connection with a colorimeter. This turbid solution was clarified with Kieselguhr and filtered through a folded filter paper, S. & S. No. 589 being used, and the funnel covered to prevent evaporation.

2. SPECIFIC ABSORPTIVE INDEX, —LOG t (COLUMNS 4 TO 7)

The magnitude of the experimental errors in the observation of the transmittancies **T** of the absorbing layer of any colored transparent solution may amount in the average to approximately 3 per cent on $-\log \mathbf{T}$, and an error of 5 per cent may be considered the extreme limit. Exceptions are to be made in the event that faintly colored solutions are investigated; for instance, the so-called "water-white" liquors of various grades or solutions of granulated sugars. The observational errors may be as great as 10 per cent in the blue end of the spectrum and even greater in the red end. The same error is, of course, transferred to the specific absorptive indexes, $-\log \mathbf{t}$. These possible observational errors may be corrected if the $-\log \mathbf{t}$ values are plotted against the wave length and a smooth curve drawn. This was not possible in this case, as the four wave lengths used were too far apart.

The specific absorptive indexes, $-\log \mathbf{t}$, are measures of the intensity of absorption, wave length by wave length, for 1 g of saccharine dry substance. Their magnitude varies with the concentration of coloring matter and with the type of coloring matter. The magnitude of the index also varies with the wave length; therefore, two different types of coloring matters will generally have different specific indexes, even if they be measured at the same wave length and have the same concentration of coloring matter per gram of dry substance. It follows, therefore, that, in general, the intensity of absorption ($-\log \mathbf{t}$) at a single wave length can not be used as a simple indicator of the relative concentrations of two different types of coloring matter.[12] Beer's law states that "the negative logarithms of the transmitted fractions are proportionate to concentration, *c*, and thickness, *b*, of the absorbing layer, *cb*. This holds for the ratios between any two $-\log$ transmittancies **T** at the same wave length for two different absorbing layers, *cb*, of the same type of solution of the same sample of sugar. The ratio between two intensities of absorption at the same wave length may, therefore, be used as a measure of the relative color concentration in the two solutions because the individual type of coloring matter is identical. However, the individual types of coloring matter vary not only with the nature of the sugar product, but also with the manner of preparing solutions of the same product. The situation is rather unusual on account of its complexity.

It follows that in the comparison of different types of sugar products valid conclusions can be drawn from specific indexes, $-\log \mathbf{t}$, at a single wave length, only in the event that several types of ratios

[12] It will be shown in a subsequent publication that measurements at the single wave length, 560 μ, may be used to determine the relative color concentrations of different types of sugar products. Wave length, 560 μ is unique in this respect.

are studied simultaneously for these products. Three different ratios should be considered in any simple analysis of the absorption spectrum of any single type [13] of coloring matter.

3. RATIOS

Three ratios in Table 1, columns 8 to 11, 12 to 15, and 17, must be calculated, if intensity and quality of absorption and the concentration of coloring matter per 1 g of saccharine dry substance are to be determined.

The ratio, R_s, between two specific absorptive indexes at the same wave length in two spectra are given in columns 8 to 11. The indexes of solution A are taken as standard of comparison. This ratio is merely a measure of differences in the intensity of absorption at any wave length, while the concentration of coloring matter remains unknown for both spectra. The ratios are calculated according to

$$R_s = \frac{(-\log \mathbf{t} \text{ of } B_a \text{ or } B_b \text{ or Turbid}) \text{ at any wave length}}{-\log \mathbf{t} \text{ of A at the same wave length}}$$

The absorption ratios, R_λ (columns 12 to 15) are measures, wave length by wave length, of the quality of absorption; that is, of the individual type of coloring matter in each individual spectrum.

$$R_\lambda = \frac{-\log \mathbf{t} \text{ at any wave length}}{-\log \mathbf{t} \text{ at wave length } 546'} \quad \begin{matrix}(\text{both } -\log \mathbf{t}\text{'s being for the same} \\ \text{solution}).\end{matrix}$$

Wave length 546 is chosen by necessity in place of $\lambda = 560$ [14] mμ because the absorption ratios must be calculated on the basis of available experimental data. As $-\log \mathbf{t}$ at $\lambda = 560$ mμ was not determined for all solutions [15] it could not be chosen as a source of comparison, and therefore the symbol Q is not used, the symbol R_λ being chosen instead in order to avoid confusion.

Column 17 gives the ratio between the specific absorptive index, $-\log \mathbf{t}$ at $\lambda = 560$ mμ (column 16) and the absorption unit, $-\log \mathbf{t}_1 = 0.00485$ at the same wave length. The latter is the measure of one unit of coloring matter of the same individual type as is contained

[13] It is well known by chemical quantitative analysis that there exists a heterogeneous mixture of many different types of coloring matters in the saccharine dry substance, and that there is a constant change in the composition of this mixture at different stages of the manufacturing process. However, the series of specific absorptive indexes, $-\log \mathbf{t}$ at any single wave length, represents the absorption of 1 g of saccharine dry substance, as if only one single caramel-like substance were present. There exist no known reactions which might be used for the separation of a $-\log$ transmissivity at a single wave length into the several $-\log$ transmittancies T of the several constituent types of coloring matters.

[14] See Color nomenclature.

[15] It could not be obtained by interpolation between the values for the mercury green, $\lambda = 546$ mμ and mercury yellow, $\lambda = 578$ mμ, because the correct method of interpolation has been worked out only in the case of transparent asbestos filtrates. This method can not, therefore, be applied with certainty to the turbid solutions here dealt with (B_a, B_b, and turbid).

in the colored spectrum of n units of coloring matter. The unknown concentration of coloring matter is therefore calculated by the ratio $\frac{-\log \mathbf{t} \text{ at } \lambda = 560 \text{ m}\mu}{-\log \mathbf{t}_1 = 0.00485}$ = units of coloring matter in 1 g saccharine dry substance. It will be noted that this ratio has been calculated only for the correctly prepared solution A.

4. ANALYSIS OF THE THREE RATIOS

(a) THE RATIO, R., FOR THE CONCENTRATED ASBESTOS FILTRATES, A, AND THE DILUTE FILTER-PAPER FILTRATE, B, TABLE 1, COLUMNS 8 TO 11 (SEE FIG. 3)

It should be noted that the ratios in columns 12 to 15 should be considered in the study of the differences in the ratios of columns 8 to 11 in order to determine whether the type of coloring matter is the same in both solutions represented by filtrates A and B.

It will be observed that either the red end or the blue end of the spectrum of solution B differs from that of the A type. Absorption is greater in the red end for solution B_a and B_b of Nos. 6 and 8, and for B_a of Nos. 14 and 15; absorption is decreased in the blue end for B_a and B_b of Nos. 6 and 8; while absorption in the blue end of B_a of Nos. 14 and 15 is greater than that of the asbestos filtrate. Absorption in the terminal blue-violet of B_a of Nos. 11 and 12, is equal to that of the A filtrate, while the difference in absorption becomes greater and greater for B_a or B_b the more the red end is approached, where the difference is greatest. A more or less uniform decrease in absorption throughout the spectrum is to be noted for sugars Nos. 9 and 10, while absorption decreases suddenly in the red end for No. 13 sugar, No. 8 showing a similar decline toward λ578 mμ.

The optical quality of all 10 B filtrates was found to be poor, as the solutions were quite turbid when examined in the dark room. It should be noted that the quantity of coloring matter in each solution was approximately equal.[16] The differences in intensities of absorption for these solutions were found to vary between 0 and ± 30 per cent for wave lengths other than 500. Most of the differences are far beyond the permissible magnitude of experimental errors. No. 15 is of special interest as the absorption of the dilute filtrate B_a with the smallest dry substance concentration indicates a greater intensity of absorption than is measured for the turbid, concentrated, unfiltered solution of No. 15. A loss by diffused light is indicated, due to an increase in the colloidal particle concentration.

The variations with the wave length in the ratios for solutions A and B lead to the general conclusion that a decided change has taken

[16] Approximate equality of coloring matter in the 10 solutions was secured by choosing equal intensity of absorption at some wave length. A $-\log \mathbf{T}$ of 0.250 at $\lambda = 500$ for thickness, $b = 12$ cm, was chosen for all solutions which then appeared of equal straw color.

place in the type of coloring matter in B. The changes appear erratic and uncontrollable, so that the method of analytical preparation for optical analysis by which the B filtrate was prepared does not appear to be trustworthy.

(*b*) THE RATIO, R_a, FOR THE CONCENTRATED, TRANSPARENT ASBESTOS FILTRATE AND THE UNFILTERED, TURBID SOLUTION, TABLE 1, COLUMNS 8 TO 11 (SEE FIG. 2)

The ratio between the absorptive indexes of these two solutions is plotted on a scale in which the index of the asbestos filtrate again appears for each sugar as equal to 1.00.

A surprising fact which is of importance to sugar technologists and sugar chemists is noted at once: The smallest differences occur for the dark colored sugar Nos. 11 to 15 and the greatest differences for the light colored sugars Nos. 6 to 10.[17] The greatest difference is noted for the lightest colored sugar, No. 6, a pale yellow, and the smallest difference for the darkest reddish-brown, No. 15.

The differences in absorption for each sugar are largest in the red end of the spectrum and decrease gradually as the blue end is approached.

It follows that filtration affects principally the red end of the spectrum. A more detailed discussion of this point will be given in a subsequent paper dealing with a study of the optical effects of various clarification and filtration media.

However, the ratio under discussion is merely an indicator of the differences between total loss of light intensity by absorption and diffusion for the turbid solution, as against total loss of light intensity by absorption for the transparent solution.[18] This difference is merely an indicator of the greater or lesser turbidity of technical sugar solutions. It is not an accurate measure of the colloidal particle concentration, the amount of diffusion, the color, or the quantity of coloring matter.

Finally, the term turbid in spectrophotometric nomenclature defines optical inhomogeneity as distinct from optical homogeneity; that is, transparency. But inasmuch as the sugar solution is a heterogeneous mixture of crystalloids, suspensoids, and emulsoids, optical homogeneity and an accurate determination of the absorption is, in general, not obtainable without a detailed study of each individual case which is beyond the limits of the present discussion. The term turbid is therefore not used as a criterion of the commercial and technical qualities of a sugar, as determination of these qualities is not as yet based upon precise spectrophotometric and ultramicroscopic

[17] No. 10 sugar is of a yellowish color, free from reddish-brown shades, while No. 11 sugar and those following appear gradually to the eye in more and more pronounced reddish-brown tints, the yellow gradually disappearing. The solutions of these sugars likewise evoke similar color sensations.

[18] The loss occasioned by diffusion becomes negligible if the solution appears suitably transparent in the dark room.

measurements. The darker colored sugar solutions appeared very clean, bright, and clear in the usual technical sense, entirely free from extraneous matter, and indicating great care in the manufacture. No. 6 solution appeared the least bright of the unfiltered solutions, an observation which is supported by the optical measurements.

(c) THE ABSORPTION RATIO, R_λ, FOR EACH INDIVIDUAL SUGAR SOLUTION. (TABLE 1, COLUMNS 12 TO 15)

Close similarity in the types of coloring matter in any two solutions is indicated if their R_λ ratios are either identical or of similar magnitude over widespread spectral regions. However, the effect of experimental error on the absorption ratio at different wave lengths should not be overlooked. For instance, an error of 3 per cent in $-\log \mathbf{t}$ at $\lambda = 436$ mμ would change the ratio, R_λ, for No. 6 sugar from 7.25 to 7.47, while the same error at $\lambda = 578$ mμ would change R_λ from 0.65 to 0.67.

At a given wave length the same absorption ratio will always be found for different concentrations of coloring matter of the same type, as long as the quality of absorption is not altered by dissociation of coloring matter; that is, as long as the validity of Lambert's-Beer's law exists. Therefore, by means of these absorption ratios it is possible to judge color qualities without the usual complications arising from differences in the concentration of coloring matter.

It will be observed in Table 1 that the ratios for any given wave length change with the method of preparation of the solution, but in a different degree for each type of colored dry substance. The differences in these ratios for the A and B solutions for a given wave length indicate a chemical effect from dilution upon the color-bearing colloidal nonsugar and consequently a change in the color of the final solution. It is to be noted that the character of the absorption in the spectrum of the B solutions differs materially from that of the standard A solution. On the other hand, there is occasionally a rather surprising similarity between the absorption ratios, R_λ, at different wave lengths of the B solutions and of the turbid solution. This is the more surprising when it is considered that the ratios of the turbid solution are those of a concentrated unfiltered solution, while those of the B solutions belong to apparently transparent dilute straw-colored solutions which have been clarified and filtered through filter paper. It may, therefore, be concluded that the method of preparing the B solutions for optical analysis is not very efficacious. The greatest increase in R_λ is noted for the final filtrate of the A solutions of the lighter colored sugars at $\lambda = 436$ mμ. The greater the efficacy of the method of clarification and filtration, the smaller will be the specific absorptive index, $-\log \mathbf{t}$, because the loss of light through diffusion by floating particles is eliminated. If,

therefore, the efficacy of clarification and filtration methods affects principally the red end of the spectrum, including $\lambda = 546$ mμ, then the lesser magnitude of $-\log \mathbf{t}$ at $\lambda = 546$ mμ will cause in turn an increase in the absorption ratios, R_λ, for the shorter wave lengths. Equality in the transparency of two solutions is therefore essential if valid conclusions are to be drawn from the relative magnitudes of these absorption ratios at the same wave length for any two sugar products. There are also noted occasional increases and decreases in R_λ for the B_a, B_b and turbid solutions relative to the A solutions. The former are due to either a coagulation or a precipitation of coloring matter, which caused a decrease in $-\log \mathbf{t}$ at $\lambda = 546$ mμ. The latter, occurring principally at $\lambda = 480$ mμ and $\lambda = 436$ mμ, are due to an increase in the magnitude of $-\log \mathbf{t}$ at $\lambda = 546$ mμ. This may be caused by the increased turbidity occasioned by excessive dilution.

Finally, it should be noted that the absorption ratios, R_λ, at a few wave lengths do not permit of a complete analysis of the optical effect produced in different solutions by different analytical methods of preparation. Neither are the deductions made in connection with these different solutions of the same product to be interpreted as an indicator of the conclusions which may be drawn in the case of transparent asbestos filtrates, A, of different types of sugar products, such as sugars, massecuites, run-offs, molasses, or liquors of various types.

The differences in the absorption ratios, R_λ, at the same wave length for solutions A and B proves that the methods of analytical preparation affect the quantity and type of coloring matter found. Inasmuch as the A filtrate is more transparent, and as the magnitude of the indexes may be confirmed for different solutions of the same product, it follows that the method of preparation of the A solution is preferable to that of the B solution.

(*d*) UNITS OF COLORING MATTER IN 1 g OF SACCHARINE DRY SUBSTANCE

The magnitude of $-\log \mathbf{t}$ at $\lambda = 560$ mμ for the transparent final asbestos filtrate, A, of each sugar, is given in column 16 and the result of converting these values into n units of coloring matter per gram of saccharine dry substance is given in column 17. The result of this conversion is, in effect, a true colorimetric analysis and it is therefore defined as the spectrocolorimetric equivalent of the index at $\lambda = 560$ mμ.

VII. APPENDIX NO. 1.—TABLE 2. DENSITIES OF SUCROSE SOLUTIONS

Column 1 gives Brix or per cent sucrose of the solution.

Column 2 gives true density; that is, the weight in vacuo of 1 cc of solution at 20° C. (Plato's table).[19]

[19] Tables 19 and 31, B. S. Circular No. 44 on Polarimetry.

Column 3 gives apparent density; that is, the weight in air with brass weights, of 1 cc of solution at 20° C. The values in this column correspond to the values of true density on the same line of column 2, having been obtained from column 2 by means of the formula

$$(1)\, M = W\left[1 + \frac{\rho}{d_2}\left(\frac{d_2 - d_1}{d_1 - \rho}\right)\right] = W\left(1 + \frac{k}{1000}\right)^{20}$$

which may be utilized for converting apparent density into true density, and vice versa, by considering that M, the weight in vacuo, and W, the apparent weight, refer to 1 cc, since true density is defined as the weight in vacuo of 1 cc and the apparent density as the weight of 1 cc of substance in air with brass weights. ρ is the density of air which has been taken as 0.0012046,[21]; d_1 the density of the solution, d_2 the density of the weights which has been taken as 8.4. The true density may be obtained from the experimentally determined apparent density by means of columns 2 and 3.

Example.—The apparent density of a 55 Brix solution is found by experiment to be 1.25651. The true density in column 2 corresponding to 1.25651 in column 3 is 1.25754.

It should be emphasized that while the relations between columns 2, 3, and 4 hold for any sugar solution, regardless of purity, the relations between these columns and column 1 holds only for pure sucrose solutions.

Column 4 gives the apparent specific gravity at 20° C. The values in this column were obtained by dividing the apparent density in column 3 by the apparent density of water at 20° C., which was taken as 0.997174.[22] The true density may be taken from column 2 on the same line as the experimentally found value of the apparent specific gravity in column 4.

Column 5 gives the grams sucrose (weighed in vacuo) per 100 cc of solution (based on columns 1 and 2).

Column 6 gives the grams of pure sucrose (weighed in air with brass weights) per 100 cc of solution (based on columns 1 and 2).

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[20] B. S. Circular No. 19, 6th ed., Table 39, p. 55.

[21] B. S. Circular No. 19, 6th ed., Table 29.

[22] B. S. Circular No. 19. J. Domke. Zeit. Ver. Deut. Zucker-Ind., 62, p. 306; 1912; O. Schrefeld, ibid, p. 312.

TABLE 2.—*Densities of pure sucrose solutions*

Brix or true per cent d. s. by weight [1]	(Plato) true density	Apparent density	Apparent specific gravity	g of sucrose per 100 cc	
				Weight in vacuo	Apparent weight in air with brass weights
1	2	3	4	5	6
40.0	1.17645	1.17541	1.17874	47.058	47.029
40.1	696	593	926	.196	.168
40.2	747	644	1.17977	.334	.306
40.3	799	695	1.18029	.473	.444
40.4	850	747	080	.611	.582
40.5	1.17901	1.17798	1.18132	.750	.721
40.6	953	849	183	47.889	.860
40.7	1.18004	901	235	48.028	47.999
40.8	056	1.17953	287	.167	48.138
40.9	108	1.18004	339	.306	.277
41.0	1.18159	1.18056	1.18390	48.445	48.416
41.1	211	107	442	.585	.555
41.2	262	159	494	.724	.695
41.3	314	211	546	.864	.834
41.4	366	263	598	49.004	48.974
41.5	1.18418	1.18314	1.18650	.143	49.114
41.6	470	356	702	.283	.254
41.7	522	418	754	.424	.394
41.8	573	470	806	.564	.534
41.9	625	522	858	.704	.674
42.0	1.18677	1.18574	1.18910	49.845	49.814
42.1	729	626	1.18962	49.985	49.955
42.2	781	678	1.19014	50.126	50.095
42.3	834	730	062	.267	.236
42.4	886	782	119	50.408	50.377
42.5	938	1.18835	1.19171	.549	50.518
42.6	990	887	224	.690	.659
42.7	1.19042	939	276	.831	.800
42.8	095	991	329	50.973	50.942
42.9	147	1.19044	381	51.114	51.083
43.0	1.19199	1.19096	1.19434	51.256	51.225
43.1	252	148	486	.398	.366
43.2	304	201	539	.539	.508
43.3	356	253	591	.681	.650
43.4	409	306	644	.824	.792
43.5	1.19462	1.19358	1.19697	51.966	51.934
43.6	514	411	749	52.108	52.076
43.7	567	483	802	.251	.219
43.8	619	516	855	.393	.362
43.9	672	569	908	.536	.504
44.0	1.19725	1.19622	1.19961	52.679	52.647
44.1	778	674	1.20013	.822	.790
44.2	830	727	066	52.965	52.933
44.3	883	780	119	53.108	53.076
44.4	936	833	172	.252	.219
44.5	1.19989	1.19886	1.20226	.395	.363
44.6	1.20042	939	279	.539	.506
44.7	095	992	332	.683	.650
44.8	148	1.20045	385	.826	.794
44.9	201	098	438	53.970	53.937
45.0	1.20254	1.20151	1.20491	54.114	54.081
45.1	307	204	545	.259	.226
45.2	360	257	598	.403	.370
45.3	414	311	651	.547	.514
45.4	467	364	705	.692	.659
45.5	1.20520	1.20417	1.20758	.837	.803
45.6	573	470	812	54.981	54.948
45.7	627	524	865	55.126	55.093
45.8	680	577	919	.272	.238
45.9	734	630	1.20972	.417	.383
46.0	1.20787	1.20684	1.21026	55.562	55.528
46.1	840	737	080	.708	.674
46.2	894	791	133	.853	.819
46.3	948	845	187	55.999	.965
46.4	1.21001	898	241	56.145	56.111
46.5	1.21055	1.20952	1.21295	.291	.256
46.6	109	1.21006	349	.437	.402
46.7	162	059	402	.583	.548
46.8	216	113	456	.729	.695
46.9	270	167	510	56.876	.841

[1] The apparent Brix—that is, g of sucrose dry substance per 100 g of solution—weighed with brass weights in air is approximately 0.01 per cent greater than the true Brix in column 7.

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	(Plato) true density	Apparent density	Apparent specific gravity	g of sucrose per 100 cc	
				Weight in vacuo	Apparent weight in air with brass weights
1	2	3	4	5	6
47.0	1.21324	1.21221	1.21564	57.022	56.988
47.1	378	275	618	.169	57.134
47.2	432	329	673	.316	.281
47.3	486	383	727	.463	.428
47.4	540	437	781	57.610	57.575
47.5	1.21594	1.21491	1.21835	57.757	57.722
47.6	648	545	889	57.904	57.869
47.7	702	599	943	58.052	58.016
47.8	756	653	1.21998	.199	.164
47.9	810	707	1.22052	.347	.312
48.0	1.21864	1.21761	1.22106	58.495	58.459
48.1	918	816	161	.643	.607
48.2	973	870	215	.791	.755
48.3	1.22027	924	270	58.939	58.903
48.4	082	979	324	59.087	59.051
48.5	1.22136	1.22033	1.22379	.236	.200
48.6	190	088	434	.385	.348
48.7	245	142	488	.533	.497
48.8	300	197	543	.682	.646
48.9	354	251	598	.831	.795
49.0	1.22409	1.22306	1.22652	59.980	59.944
49.1	463	360	707	60.129	60.093
49.2	518	415	762	.279	.242
49.3	573	470	817	.428	.392
49.4	627	525	872	.578	.541
49.5	1.22682	1.22580	1.22927	.728	.691
49.6	737	634	1.22982	60.878	841
49.7	792	689	1.23037	61.028	60.990
49.8	847	744	092	.178	61.141
49.9	902	799	147	61.328	61.292
50.0	1.22956	1.22854	1.23202	61.478	61.441
50.1	1.23012	909	1.23257	.629	.591
50.2	067	1.22964	313	.780	.742
50.3	122	1.23019	368	.930	61.893
50.4	177	074	423	62.081	62.043
50.5	1.23232	1.23130	1.23478	.232	.194
50.6	287	185	534	.383	.345
50.7	343	240	589	.535	.497
50.8	398	295	645	.686	.648
50.9	453	351	700	.838	.799
51.0	1.23508	1.23406	1.23756	62.989	62.951
51.1	564	461	811	63.141	63.103
51.2	619	517	867	.293	.255
51.3	675	572	922	.445	.407
51.4	730	628	1.23978	.597	.559
51.5	1.23786	1.23683	1.24034	.750	.711
51.6	841	739	089	.902	63.863
51.7	897	794	145	64.055	64.016
51.8	953	850	201	.208	.168
51.9	1.24008	906	257	.360	.321
52.0	1.24064	1.23962	1.24313	64.513	64.474
52.1	120	1.24017	369	.666	.627
52.2	176	073	425	.820	.780
52.3	232	129	481	.973	64.934
52.4	287	185	537	65.127	65.087
52.5	1.24343	1.24241	1.24593	65.280	65.240
52.6	399	297	649	.433	.393
52.7	455	353	705	.588	.548
52.8	511	409	761	.742	.702
52.9	567	465	818	.896	65.856
53.0	1.24623	1.24521	1.24874	66.050	66.010
53.1	680	577	930	.205	.164
53.2	736	633	987	.359	.319
53.3	792	690	1.25043	.514	.474
53.4	848	746	099	.669	.628
53.5	1.24905	1.24802	1.25156	.824	.783
53.6	961	858	212	.979	66.938
53.7	1.25017	915	269	67.134	67.093
53.8	074	971	325	.290	.249
53.9	130	1.25028	382	.445	.404

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	(Plato) true density	Apparent density	Apparent specific gravity	g of sucrose per 100 cc	
				Weight in vacuo	Apparent weight in air with brass weights
1	2	3	4	5	6
54.0	1.25187	1.25084	1.25439	67.601	67.560
54.1	243	141	495	.757	.715
54.2	300	197	552	.912	67.871
54.3	356	254	609	68.069	68.027
54.4	413	311	666	.225	.183
54.5	1.25470	1.25367	1.25723	.381	.339
54.6	526	424	780	.537	.496
54.7	583	481	836	.694	.652
54.8	640	538	893	.851	.809
54.9	697	594	950	69.008	68.965
55.0	1.25754	1.25651	1.26007	69.164	69.122
55.1	810	708	064	.322	.279
55.2	867	765	122	.479	.436
55.3	924	822	179	.636	.594
55.4	982	879	236	.794	.751
55.5	1.26039	1.25936	1.26293	69.951	69.909
55.6	096	1.25993	350	70.109	70.066
55.7	153	1.26050	408	.267	.224
55.8	210	108	465	.425	.382
55.9	267	165	522	.583	.540
56.0	1.26324	1.26222	1.26580	70.742	70.698
56.1	382	279	637	70.900	70.857
56.2	439	337	695	71.059	71.015
56.3	496	394	752	.217	.174
56.4	554	452	810	.376	.333
56.5	1.26611	1.26509	1.26868	.535	.492
56.6	669	566	925	.694	.651
56.7	726	624	1.26983	71.854	.810
56.8	784	682	1.27041	72.013	71.969
56.9	841	739	098	.173	72.129
57.0	1.26899	1.26797	1.27156	72.332	72.288
57.1	956	854	214	.492	.448
57.2	1.27014	912	272	.652	.608
57.3	072	970	330	.812	.768
57.4	130	1.27028	388	72.973	72.928
57.5	1.27188	1.27086	1.27446	73.133	73.088
57.6	246	143	504	.293	.249
57.7	304	201	562	.454	.409
57.8	361	259	620	.615	.570
57.9	419	317	678	.776	.731
58.0	1.27477	1.27375	1.27736	73.937	73.892
58.1	535	433	794	74.098	74.053
58.2	594	492	853	.260	.214
58.3	652	550	911	.421	.375
58.4	710	608	1.27969	.583	.537
58.5	1.27768	1.27664	1.28028	.744	.699
58.6	826	724	086	74.906	74.860
58.7	884	782	145	75.068	75.022
58.8	943	841	203	.230	.184
58.9	1.28001	899	262	.393	.346
59.0	1.28060	1.27958	1.27320	75.555	75.509
59.1	118	1.28016	379	.717	.671
59.2	176	074	437	75.880	.834
59.3	235	133	496	76.043	75.997
59.4	294	191	555	.206	76.160
59.5	1.28352	1.28250	1.27614	.370	.323
59.6	411	309	672	.533	.486
59.7	469	367	731	.696	.649
59.8	528	426	790	76.860	.813
59.9	587	485	849	77.024	76.976
60.0	1.28646	1.28544	1.28908	77.187	77.140

VIII. APPENDIX NO. 2.—METHOD OF OBTAINING −LOG T

Log **T** for values of **T** from **T**=1.00 to **T**=0.100 may be taken directly from the table of mantissas. For this range the characteristic is zero. Log **T** for values of **T** between **T**=0.100 and **T**=0.0000 is obtained by taking from the table of mantissas the decimal part of the logarithm corresponding to the number without regard to the position of the decimal point in the number and adding thereto the appropriate characteristic.

It should be remembered that if **T** is expressed as the fractional part of unity the characteristic is equal to minus the number of zeros between the decimal point and the first significant figure. Thus, the characteristic of **T**=0.5 is 0; that of **T**=0.005 (0.5 per cent) is −2; etc.

EXAMPLE 1.—To find −log **T** if **T**=0.00543. In the table of mantissas the mantissa corresponding to 543 (disregarding the position of the decimal point) is −0.26520. Since there are two zeros between the decimal point and the first significant figure the characteristic is −2. Adding these, log **T**= −2.26520 and −log **T**= +2.2652.

TABLE 3.—*Mantissas for numbers from 0 to 1*

T	0	1	2	3	4	5	6	7	8	9
0.10	−0.00000	−0.99568	−0.99140	−0.98716	−0.98297	−0.97881	−0.97469	−0.97062	−0.96658	−0.96257
.11	−.95861	−.95468	−.95078	−.94692	−.94310	−.93930	−.93554	−.93181	−.92812	−.92445
.12	−.92082	−.91721	−.91364	−.91009	−.90658	−.90309	−.89963	−.89620	−.89279	−.88941
.13	−.88606	−.88273	−.87943	−.87615	−.87290	−.86967	−.86646	−.86328	−.86012	−.85699
.14	−.85387	−.85078	−.84771	−.84466	−.84164	−.83863	−.83565	−.83268	−.82974	−.82681
.15	−.82391	−.82102	−.81816	−.81531	−.81248	−.80967	−.80688	−.80410	−.80134	−.79860
.16	−.79588	−.79317	−.79048	−.78781	−.78516	−.78252	−.77989	−.77728	−.77469	−.77211
.17	−.76955	−.76700	−.76447	−.76195	−.75945	−.75696	−.75449	−.75203	−.74958	−.74715
.18	−.74473	−.74232	−.73993	−.73755	−.73518	−.73283	−.73049	−.72816	−.72584	−.72354
.19	−.72125	−.71897	−.71670	−.71444	−.71220	−.70992	−.70774	−.70553	−.70333	−.70115
.20	−.69897	−.69680	−.69465	−.69250	−.69037	−.68825	−.68613	−.68403	−.68194	−.67985
.21	−.67778	−.67572	−.67566	−.67162	−.66959	−.66756	−.66555	−.66354	−.66154	−.65956
.22	−.65758	−.65561	−.65365	−.65170	−.64975	−.64782	−.64589	−.64397	−.64207	−.64016
.23	−.63827	−.63639	−.63451	−.63264	−.63078	−.62893	−.62709	−.62525	−.62342	−.62160
.24	−.61979	−.61798	−.61618	−.61439	−.61261	−.61083	−.60906	−.60730	−.60555	−.60380
.25	−.60206	−.60033	−.59860	−.59688	−.59517	−.59346	−.59176	−.59007	−.58838	−.58670
.26	−.58503	−.58336	−.58170	−.58004	−.57840	−.57675	−.57512	−.57349	−.57187	−.57025
.27	−.56864	−.56703	−.56543	−.56384	−.56225	−.56067	−.55909	−.55752	−.55596	−.55440
.28	−.55284	−.55129	−.54975	−.54821	−.54668	−.54516	−.54363	−.54212	−.54061	−.53910
.29	−.53760	−.53611	−.53462	−.53313	−.53165	−.53018	−.52871	−.52724	−.52578	−.52433
.30	−.52288	−.52143	−.51999	−.51856	−.51713	−.51570	−.51428	−.51286	−.51145	−.51004
.31	−.50864	−.50724	−.50585	−.50446	−.50307	−.50169	−.50031	−.49894	−.49757	−.49621
.32	−.49485	−.49349	−.49214	−.49080	−.48945	−.48812	−.48678	−.48545	−.48413	−.48280
.33	−.48149	−.48017	−.47886	−.47756	−.47625	−.47496	−.47366	−.47237	−.47108	−.46980
.34	−.46852	−.46725	−.46597	−.46471	−.46344	−.46218	−.46092	−.45967	−.45842	−.45717
.35	−.45593	−.45469	−.45346	−.45223	−.45100	−.44977	−.44855	−.44733	−.44612	−.44491
.36	−.44370	−.44249	−.44129	−.44009	−.43890	−.43771	−.43652	−.43533	−.43415	−.43297
.37	−.43180	−.43063	−.42946	−.42829	−.42713	−.42597	−.42481	−.42366	−.42251	−.42136
.38	−.42022	−.41908	−.41794	−.41680	−.41567	−.41454	−.41341	−.41229	−.41117	−.41005
.39	−.40894	−.40782	−.40671	−.40561	−.40450	−.40340	−.40230	−.40121	−.40012	−.39903
.40	−.39794	−.39686	−.39577	−.39469	−.39362	−.39254	−.39147	−.39041	−.38934	−.38828
.41	−.38722	−.38616	−.38510	−.38405	−.38300	−.38195	−.38091	−.37986	−.37882	−.37779
.42	−.37675	−.37572	−.37469	−.37366	−.37263	−.37161	−.37059	−.36957	−.36856	−.36754
.43	−.36653	−.36552	−.36452	−.36351	−.36251	−.36151	−.36051	−.35952	−.35853	−.35754
.44	−.35655	−.35556	−.35458	−.35360	−.35262	−.35164	−.35067	−.34969	−.34872	−.34775

TABLE 3.—*Mantissas for numbers from 0 to 1*—Continued

T	0	1	2	3	4	5	6	7	8	9
0.45	−0.34679	−0.34582	−0.34486	−0.34390	−0.34294	−0.34199	−0.34104	−0.34008	−0.33913	−0.33819
.46	−.33724	−.33630	−.33536	−.33442	−.33348	−.33255	−.33161	−.33068	−.32975	−.32883
.47	−.32790	−.32698	−.32606	−.32514	−.32422	−.32331	−.32239	−.32148	−.32057	−.31966
.48	−.31876	−.31785	−.31695	−.31605	−.31515	−.31426	−.31336	−.31247	−.31158	−.31069
.49	−.30980	−.30892	−.30803	−.30715	−.30627	−.30539	−.30452	−.30364	−.30277	−.30190
.50	−.30103	−.30016	−.29930	−.29843	−.29757	−.29671	−.29585	−.29499	−.29416	−.29328
.51	−.29243	−.29158	−.29073	−.28988	−.28904	−.28819	−.28735	−.28651	−.28567	−.28483
.52	−.28400	−.28316	−.28233	−.28150	−.28067	−.27984	−.27901	−.27819	−.27737	−.27654
.53	−.27572	−.27491	−.27409	−.27327	−.27246	−.27165	−.27084	−.27003	−.26922	−.26841
.54	−.26761	−.26680	−.26600	−.26520	−.26440	−.26360	−.26281	−.26201	−.26122	−.26043
.55	−.25964	−.25885	−.25806	−.25727	−.25649	−.25571	−.25493	−.25414	−.25337	−.25259
.56	−.25181	−.25104	−.25026	−.24949	−.24872	−.24795	−.24718	−.24642	−.24565	−.24489
.57	−.24413	−.24336	−.24260	−.24185	−.24109	−.24033	−.23958	−.23882	−.23807	−.23732
.58	−.23657	−.23582	−.23508	−.23433	−.23359	−.23284	−.23210	−.23136	−.23062	−.22988
.59	−.22915	−.22841	−.22768	−.22695	−.22621	−.22548	−.22475	−.22403	−.22330	−.22257
.60	−.22185	−.22113	−.22040	−.21968	−.21896	−.21824	−.21753	−.21681	−.21610	−.21538
.61	−.21467	−.21396	−.21325	−.21254	−.21183	−.21112	−.21042	−.20971	−.20901	−.20831
.62	−.20761	−.20691	−.20621	−.20551	−.20482	−.20412	−.20343	−.20273	−.20204	−.20135
.63	−.20066	−.19997	−.19928	−.19860	−.19791	−.19723	−.19654	−.19586	−.19518	−.19450
.64	−.19382	−.19314	−.19246	−.19179	−.19111	−.19044	−.18977	−.18910	−.18842	−.18776
.65	−.18709	−.18642	−.18575	−.18509	−.18442	−.18376	−.18310	−.18243	−.18177	−.18111
.66	−.18046	−.17980	−.17914	−.17849	−.17783	−.17718	−.17653	−.17587	−.17522	−.17457
.67	−.17393	−.17328	−.17263	−.17198	−.17134	−.17070	−.17005	−.16941	−.16877	−.16813
.68	−.16749	−.16685	−.16622	−.16558	−.16494	−.16431	−.16368	−.16304	−.16241	−.16178
.69	−.16115	−.16052	−.15989	−.15927	−.15864	−.15802	−.15739	−.15677	−.15614	−.15552
.70	−.15490	−.15428	−.15366	−.15304	−.15243	−.15181	−.15120	−.15058	−.14997	−.14935
.71	−.14874	−.14813	−.14752	−.14691	−.14630	−.14569	−.14509	−.14448	−.14388	−.14327
.72	−.14267	−.14206	−.14146	−.14086	−.14026	−.13966	−.13906	−.13847	−.13787	−.13727
.73	−.13668	−.13608	−.13549	−.13490	−.13430	−.13371	−.13312	−.13253	−.13194	−.13136
.74	−.13077	−.13018	−.12960	−.12901	−.12843	−.12784	−.12726	−.12668	−.12610	−.12552
.75	−.12494	−.12436	−.12378	−.12321	−.12263	−.12205	−.12148	−.12090	−.12033	−.11976
.76	−.11919	−.11862	−.11805	−.11748	−.11691	−.11634	−.11577	−.11520	−.11464	−.11407
.77	−.11351	−.11295	−.11238	−.11182	−.11126	−.11070	−.11014	−.10958	−.10902	−.10846
.78	−.10791	−.10735	−.10679	−.10624	−.10568	−.10513	−.10458	−.10403	−.10347	−.10292
.79	−.10237	−.10182	−.10127	−.10073	−.10018	−.09963	−.09909	−.09864	−.09799	−.09745
.80	−.09691	−.09637	−.09583	−.09528	−.09474	−.09420	−.09366	−.09313	−.09259	−.09205
.81	−.09151	−.09098	−.09046	−.08991	−.08939	−.08884	−.08831	−.08778	−.08725	−.08672
.82	−.08619	−.08566	−.08513	−.08460	−.08407	−.08355	−.08302	−.08249	−.08197	−.08145
.83	−.08092	−.08040	−.07988	−.07935	−.07883	−.07831	−.07779	−.07727	−.07676	−.07624
.84	−.07572	−.07520	−.07469	−.07417	−.07366	−.07314	−.07263	−.07212	−.07160	−.07109
.85	−.07058	−.07007	−.06956	−.06905	−.06854	−.06803	−.06753	−.06702	−.06651	−.06601
.86	−.06550	−.06500	−.06449	−.06399	−.06349	−.06298	−.06248	−.06198	−.06148	−.06098
.87	−.06048	−.05998	−.05948	−.05899	−.05849	−.05799	−.05750	−.05700	−.05651	−.05601
.88	−.05552	−.05502	−.05453	−.05404	−.05355	−.05306	−.05257	−.05208	−.05159	−.05110
.89	−.05061	−.05012	−.04964	−.04915	−.04866	−.04818	−.04769	−.04721	−.04672	−.04624
.90	−.04576	−.04528	−.04479	−.04431	−.04383	−.04335	−.04287	−.04239	−.04191	−.04144
.91	−.04096	−.04048	−.04001	−.03953	−.03905	−.03858	−.03810	−.03763	−.03716	−.03668
.92	−.03621	−.03574	−.03527	−.03480	−.03433	−.03386	−.03339	−.03292	−.03245	−.03198
.93	−.03152	−.03105	−.03058	−.03012	−.02965	−.02919	−.02872	−.02826	−.02780	−.02733
.94	−.02687	−.02641	−.02595	−.02549	−.02503	−.02457	−.02411	−.02365	−.02319	−.02273
.95	−.02228	−.02182	−.02136	−.02091	−.02045	−.02000	−.01954	−.01909	−.01863	−.01818
.96	−.01773	−.01728	−.01682	−.01637	−.01592	−.01547	−.01502	−.01457	−.01412	−.01368
.97	−.01323	−.01278	−.01233	−.01189	−.01144	−.01100	−.01055	−.01011	−.00966	−.00922
.98	−.00877	−.00833	−.00789	−.00745	−.00700	−.00656	−.00612	−.00568	−.00524	−.00480
.99	−.00436	−.00393	−.00349	−.00305	−.00261	−.00218	−.00174	−.00130	−.00087	−.00043

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